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EVALUATION OF CONTAINER MATERIALS FOR ZIRCEX
AND DAREX NUCLEAR-FUEL-RECOVERY PROCESSES

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EVALUATION OF CONTAINER MATERIALS FOR ZIRCEX AND DAREX NUCLEAR-FUEL-RECOVERY PROCESSES

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and Frederick W. Fink

The selection of a suitable material for the processing equipment is most important in fuel-recovery processes. The problem arises because of the aggressive nature of the reagents that must be used for disintegrating or dissolving some spent fuel elements. In this investigation, corrosion tests were made under conditions simulating those that may occur in several proposed processes in order that candidate materials of construction could be evaluated.

No material has been found which would allow both the hydrochlorination and dissolution steps of the vapor-phase Zircex process to be carried out in a single vessel. For a two-vessel process, several materials, such as Inconel, Haynes 25, Type S-816 alloy, Illium R, and the Hastelloys B and C, appear promising for construction of a hydrochlorinator; the dry residue would then be transferred to another vessel, perhaps of titanium or tantalum, for dissolution.

In the alternate liquid-phase Zircex process, preliminary tests have given promising results with nickel and nickel-chromium alloys. However, the only metals studied, which withstand the corrosive boiling $\text{AlCl}_3\text{-NH}_4\text{Cl}$ plus gaseous HCl environment with but negligible weight losses have been platinum, gold, tungsten, and molybdenum.

A variety of laboratory studies have shown that titanium will apparently withstand any condition likely to occur in the critical areas of the Darex process, including the dissolver and chloride-stripping column. It will undergo a severe attack in HCl vapor, but this is easily prevented by the presence of a small amount of nitric acid vapor or oxides of nitrogen. Tantalum is another promising material disclosed by these tests, but its use in the dissolver seems negated because embrittlement was detected under certain conditions.

No signs of cracking or other attack have been observed on Type 347 stainless steel specimens exposed at room temperature with various levels of stress for over 6 months to Purex-type acid extraction systems containing chlorides far in excess of the concentrations expected during operation of either the Zircex or Darex head-end processes.

INTRODUCTION

Various processes are now under study at several AEC sites for the separation of the fissionable materials from the fission products in spent power-reactor fuel elements. Two of these processes, the Zircex and the Darex, may be used as head-end methods for making uranium available in a nitrate solution suitable for solvent extraction by conventional means. The Zircex process will handle fuel elements containing zirconium as a cladding or diluent, while elements containing stainless steel would be rendered soluble in the Darex process by dilute aqua regia, from which the name for the process is derived. These and other processes for the recovery of spent fuel elements are being

developed by the Chemical Technology Division of the Oak Ridge National Laboratory and have been described in the literature.⁽¹⁾ The corrosion evaluation of materials of construction for these processes is being carried out by Battelle Memorial Institute as part of a program of assistance to the Chemical Technology Division.

THE ZIRCEX PROCESSES

Use is made of the volatility of zirconium tetrachloride to separate uranium from zirconium alloy or cladding in the Zircex processes. In one proposed operation, the hydrochlorination could be effected by means of HCl gas in a gas-phase type of reaction conducted at 300 to 600 C. The volatile $ZrCl_4$ would be removed and the UCl_3 dissolved in water or nitric acid. The resulting solution, after chloride stripping and proper adjustment, would be handled by the usual methods for solvent extraction in order that the uranium values might be reclaimed.

An alternate liquid-phase hydrochlorination process has been proposed. Elements would be dissolved and hydrochlorinated in a refluxing low-melting coordination compound such as $AlCl_3 \cdot NH_4Cl$, using HCl gas at about 400 C. The volatile $ZrCl_4$ would sublime. The melt would then be distilled to recover the aluminum and ammonium chlorides and the residual uranium and other nonvolatile metal chlorides would be dissolved in water and nitric acid in preparation for solvent extraction.

Gas-Phase Hydrochlorination

The Dissolution Step

From a technical and economic viewpoint, it would be preferable if the dissolution of the metallic or metal chloride residue, following the gas-phase hydrochlorination, could be carried out in the same reaction vessel. Accordingly, fairly extensive investigations have been undertaken to evaluate materials for the construction of such a vessel. With the requirements of the hydrochlorination step in mind, 15 likely materials were chosen and screened in preliminary tests under conditions approximating those of the dissolution step. Boiling solutions, whose compositions simulated those that could occur at various stages during the dissolution, were used. The solution compositions can be found listed on Figures 1, 2, and 3.

The approximate composition of the materials above which were screened and others which were considered in the program are given in Table 1. Specimens of each candidate were exposed at the boiling liquid, interface, and vapor positions in units consisting of Erlenmeyer flasks topped by water-cooled Allihn condensers operated with continuous refluxing. The specimens were usually removed at weekly intervals, washed and scrubbed free of any easily removable corrosion products, and weighed. The loss in weight was then converted to a corrosion rate, expressed as average penetration in mils per month. Visual examination also was made at the time of weighing. Usually the acid solution was renewed before replacing the specimens for another exposure period.

(1) References at end.

FIGURE 1. CORROSION RESULTS IN 0.5 M ZIRCEX SOLUTIONS (BOILING)

4 weeks of exposure unless noted otherwise.

FIGURE 2. CORROSION RESULTS IN 3 M ZIRCEX SOLUTIONS (BOILING)

4 weeks of exposure unless noted otherwise.

A-22324

FIGURE 3. CORROSION RESULTS IN 5 M ZIRCEX SOLUTIONS (BOILING)

4 weeks of exposure unless noted otherwise.

TABLE 1. COMPOSITION OF CANDIDATES CONSIDERED FOR MATERIALS OF CONSTRUCTION

Metal	Symbol	Nominal Composition, w/o											
		Co	Cr	Ni	Fe	Mn	Mo	Cu	Si	W	C	Nb	B
Tantalum	TA	--	--	--	--	--	--	--	--	--	--	--	--
Titanium	TI	--	--	--	--	--	--	--	--	--	--	--	--
Vitallium	VIT	62.2	27.4	2.8	0.7	0.66	5.5	--	0.53	--	0.22	--	--
Haynes 21		62.0	28.0	2.5	2.0 max	--	5.2	--	--	--	0.30	--	--
Haynes 23		64.6	26.0	1.5 max	2.0 max	--	--	--	--	5.5	0.40	--	--
Haynes 25	H25	50.4	20.0	10.0	2.0 max	1.5	--	--	1.0 max	15.0	0.15 max	--	--
Haynes 30		50.6	26.0	15.0	2.0 max	--	6.0	--	--	--	0.40	--	--
Haynes 36		52.8	18.5	10.0	2.0 max	1.3	--	--	0.50	14.5	0.40	--	0.03
Type S-816	S816	44.7	19.0	20.0	3.0	0.6	4.0	--	0.3	4.0	0.40	4.0	--
Type S-590	S590	20.0	19.7	20.0	26.0	2.0	3.7	--	1.0 max	3.75	0.45	3.75	--
Carpenter 20	C20	--	20.0	29.0	44.2	0.75	2.0	3.0	1.0	--	0.07	--	--
Carpenter 20 stabilized	C20S	--	20.0	29.0	43.6	0.75	2.0	3.0	1.0	--	--	0.7	--
Type 304 stainless	304	--	19.0	9.5	68.4	2.0	--	--	1.0	--	0.08	--	--
Hastelloy X		--	22.0	45.0	23.9	--	9.0	--	--	--	0.15 max	--	--
Hastelloy F		2.5	22.0	45.0	21.0	1.5 5	6.0	--	1.0	1.0	--	--	--
Hastelloy C	HAC	2.5 max	15.5	54.6	5.5	1.0	16.0	--	1.0	3.8	0.08	--	--
Illium R	ILR	--	22.0	63.8	2.5	1.0	6.5	4.0	--	--	0.20	--	--
Inconel		--	15.5	76.2	7.5	0.25	--	0.2	0.25	--	0.08	--	--
"A" Nickel	NIA	--	--	99.4	--	--	--	--	--	--	--	--	--
Monel		--	--	67.2	1.5	1.0	--	30.0	0.1	--	0.15	--	--
Nichrome V		--	19.0	75.8	1.0 max	2.5 max	--	--	1.5	--	0.25 max	--	--
Hastelloy B		--	--	65.0	5.0	1.0 0	28.0	--	1.0	--	--	--	--
Hastelloy W		--	6.0	61.5	5.5	1.0	25.0	--	1.0	--	--	--	--

A limiting value of 3 mils per month was arbitrarily chosen for the maximum allowable corrosion rate before the testing of a material was discontinued. On this basis, over half of the candidate materials were eliminated from further consideration. The corrosion rates for those materials showing the best resistance to corrosion are summarized in Table 2. The extent of the corrosion, measured following 4 weeks of exposure, is shown in Figures 1, 2, and 3, while the appearance of the specimens at the conclusion of the tests, along with the final corrosion rates, can be found in Figures 4, 5, and 6. The symbols used for column headings in Figures 4, 5, and 6 refer to the designations shown in Table 1.

The candidate materials were also evaluated in boiling solutions of 15 M HNO_3 , 0.4 M $\text{UO}_2(\text{NO}_3)_2$ through which HCl gas was bubbled. Since the flow of HCl tended to deplete these solutions in HNO_3 , the materials were exposed in a gradually changing environment. For example, at the HCl flow rate used, nitrate ion was completely expelled from the solution after several weeks and the chloride concentration increased until the approximate composition of azeotropic HCl was reached.

Some representative results from this series of elimination tests are given in Table 3. Only corrosion data prior to depletion of nitrates in the bath are recorded. Specimens of tantalum showed small weight gains, indicating negligible corrosion. Carpenter 20 showed good resistance in these elimination tests but performed poorly during subsequent cyclic tests when cycled into somewhat similar solutions. Carpenter 20 stabilized, not shown, had slightly higher corrosion rates. Specimens of as-cast Haynes 21 were soon disqualified from the test, but specimens cut from pieces of Haynes 21, rolled at Battelle, showed reasonable corrosion rates even after 8 weeks of exposure.

Specimens of 75A titanium, the titanium-6 w/o aluminum-4 w/o vanadium alloy, and those of RC-55 titanium ran for several weeks with only negligible weight losses. Nitrate ion was still detectable in these solutions at the end of the exposure periods. However, in other tests with titanium and in a test with Type S-816 specimens, a severe attack leading to a rapid failure of the specimens occurred suddenly during the fourth week of exposure. Only low corrosion rates had been measured up to the time of failure. Analyses of the solutions remaining from these tests showed that the nitrate ion had been completely expelled. It has never been possible to detect nitrates in any of the solutions remaining after the severe attack of titanium. The color of these solutions indicates that there may be a correlation between the oxidation potential necessary for the passivation of titanium and that required for the oxidation of uranium to the hexavalent state. However, this has not been substantiated.

Thus, it has been concluded that any contemplated utilization of titanium must, of necessity, provide adequate oxidizing conditions to maintain the metal in a passive state; otherwise, catastrophic failure can occur. These conclusions have been further confirmed by tests in simulated Zircex and Darex chloride-stripper solutions which will be described later.

Experiments of a preliminary nature have indicated that probably a fairly small nitrate concentration (perhaps a fraction of a mole per liter) is all that is necessary to provide adequate oxidizing conditions, but, so far, the nitrate concentration necessary has not been accurately defined.

TABLE 2. MATERIALS PASSING THE ZIRCEX ELIMINATION TESTS

Zircex Test	Material (Arranged in Order of Decreasing Resistance)
0.5 M	Titanium Tantalum Type S-816 Haynes 25 Vitallium Hastelloy C
3 M	Tantalum Titanium Vitallium Type S-816 Carpenter 20 Type S-590 Haynes 25 Carpenter 20 stabilized
5 M	Tantalum Titanium Vitallium Type S-816 Type S-590

ALLOY : TA TI VIT H25 S816 S590 C20 C20S ILR HAC 304 HAB NIA

HOURS : 658 658 669 669 655 669 168 168 331 669 4 3 4

N39758

FIGURE 4. SPECIMENS FOLLOWING EXPOSURE IN 0.5 M ZIRCEX SOLUTIONS (BOILING)

ALLOY .	TA	TI	VIT	H 25	S816	S590	C20	C20S	ILR	HAC	304	INC	HAB	NIA
HOURS	674	674	661	662	674	662	662	662	506	161	3	3	3	3
V A P O R		NOT AVAILABLE
MIL/MO WT GAIN	0.01	0.04	0.20	0.13	0.08	0.10	0.05	0.61	1.84	181.20	328.00	423.9	595.8	
I N T E R F A C E		NOT AVAILABLE
MIL/MO WT GAIN	0.02	0.15	0.39	0.28	0.32	0.35	0.47	188.7	12.10	2419.80	3273.70	3557.9	5192.4	
L I Q U I D		NOT AVAILABLE
MIL/MO WT GAIN	0.01	0.15	0.47	0.34	0.42	0.37	1.04	18.52	14.52	177.10	4550.70	11173.9	7141.2	

CUT OUT

N39761

FIGURE 5. SPECIMENS FOLLOWING EXPOSURE IN 3 M ZIRCEX SOLUTIONS (BOILING)

ALLOY:		<u>TA</u>	<u>TI</u>	<u>VIT</u>	<u>H25</u>	<u>S816</u>	<u>S590</u>	<u>C20</u>	<u>C20S</u>	<u>ILR</u>	<u>HAC</u>	<u>304</u>	<u>HAB</u>	<u>NIA</u>
HOURS :		13 32	1332	1326	160	1332	1302	160	160	162	160	!	!	!
V A P O R

MIL/MO	0.00	0.20	008	0.96	0.63	1.28	27.88	77.11	11.41	15.89				
I N T E R F A C E

MIL/MO	0.00	0.01	037	8.42	1.49	2.92	6.32	2.09	92.14	39.40				
L I Q U I D

MIL/MO	0.00	0.01	0.42	1.60	1.88	2.54	2.11	2.62	105.97	49.84				

N39759

FIGURE 6. SPECIMENS FOLLOWING EXPOSURE IN 5 M ZIRCEX SOLUTIONS (BOILING)

TABLE 3. REPRESENTATIVE CORROSION RESULTS IN 15 M
(STARTING COMPOSITION) BOILING
ZIRCEX SOLUTIONS

HCl gas bubbled through solutions continuously.

Specimen	Specimen Position	Corrosion Rate for Indicated Exposure, mils per month				Remarks
		1 Week	2 Weeks	3 Weeks	4 Weeks	
Tantalum	Vapor	g	g	g	g	
	Interface	g	g	g	g	
	Liquid	g	g	g	g	
Carpenter 20	Vapor	1.3	0.9	1.3	1.6	
	Interface	1.2	0.9	1.1	1.3	
	Liquid	1.2	1.1	1.3	1.4	
Haynes 21 (as cast)	Vapor	1.1	1.7	--	--	
	Interface	1.2	6.7	--	--	
	Liquid	1.8	31.0	--	--	
Haynes 21 (rolled)	Vapor	0.9	0.9	1.0	1.1	Rates essentially un- changed after 8 weeks of exposure
	Interface	1.2	1.1	1.2	1.2	
	Liquid	1.3	1.9	2.0	2.0	
Titanium (75A)	Vapor	0.0	0.0	g	g	Rates essentially un- changed after 16 weeks of exposure
	Interface	g	g	g	g	
	Liquid	g	g	g	g	
Ti-6 w/o Al-4 w/o V	Vapor	g	g	g	g	Rates essentially un- changed after 16 weeks of exposure
	Interface	g	g	g	g	
	Liquid	g	g	g	g	
Titanium (RC-55)	Vapor	g	0.1	0.1	Failed rapidly	
	Interface	0.0	0.2	0.2	g	
	Liquid	0.0	0.5	0.5	0.3	
Type S-816	Vapor	1.6	1.8	1.7	Failed rapidly	
	Interface	2.0	2.4	2.5	Ditto	
	Liquid	1.8	2.7	3.1	4.1	

Note: g indicates a very small gain in weight of the specimen during the exposure. The starting composition of these solutions was 15.0 M HNO₃, 0.4 M UO₂ (NO₃)₂.

To provide additional information along these lines, a series of experiments was conducted to examine the corrosive or passivating action of various gases on titanium in azeotropic HCl solutions. The gases N_2O , NO, NO_2 , NOCl, and chlorine were passed singly through a system containing boiling 6 M HCl. In one test, pieces of 75A titanium were placed at the vapor, interface, and liquid positions in the flask and the gas bubbled through the solution. In the other tests, the specimens were exposed in the vapor only and the gas was passed above the solution.

Table 4 summarizes the corrosion rates for the titanium specimens exposed in the liquid and vapor positions. It can be seen that the corrosion rates were high and approximately the same for specimens exposed to N_2O and NO as for those exposed to azeotropic HCl.

The corrosion of vapor-phase specimens was inhibited almost completely by NO_2 and chlorine. The NO_2 also imparted a considerable amount of inhibition to the liquid-phase specimens. Chlorine showed no inhibition with liquid-phase specimens.

Other tests showed that the presence of uranium in azeotropic HCl will inhibit the corrosion of titanium specimens submerged in the boiling liquid. This would account for the resistance of the specimens to the liquid phase during catastrophic attack of the specimens exposed in the vapor phase.

The hydrochlorination of certain fuels, such as those with a UO_2 core, may leave a low-chloride residue after volatilization of the $ZrCl_4$. Materials for such service were evaluated in boiling solutions of 5 M HNO_3 , 0.4 M $UO_2(NO_3)_2$, containing 500 ppm chloride. Tantalum, titanium, Vitallium, Haynes 25, Type S-816, Type S-590, Carpenter 20, Carpenter 20 stabilized, and Types 347 and 304 ELC stainless steel showed rates of less than 1 mil per month at an exposure time of about 4000 hr.

Another of the proposed dissolution steps following hydrochlorination would use water as the solvent, ending with a solution of UCl_3 . Elimination tests were run in boiling solutions of 0.4 M UCl_3 . None of the five materials considered for such a system withstood the attack for even 1 week. These materials were Carpenter 20, Haynes 21, and Type S-816 alloys, and Type 304 ELC and Type 316 stainless steels. Serious stress-corrosion cracking was shown by the Type 316 stainless and S-816 specimens at cut edges and stencil marks. Figure 7 shows the appearance of the specimens at the conclusion of the experiments and includes values for the corrosion rates.

Cyclic Tests for Both Hydrochlorination and Dissolution Steps

As was mentioned before, the gas-phase Zircex process involves two widely different steps. In the first, the fuel element would be treated by HCl gas at about 600 C. Following complete hydrochlorination of the bundle, the salts would be removed by treatment with nitric acid solutions. Both steps of this process would preferably be carried out in the same vessel. If materials cannot be found to withstand such severe conditions, it will be necessary to carry out each step in independent vessels.

An experimental program has been under way with the objective of determining optimum container materials for each possible process mentioned above. The program was arranged so that the specimens were alternately exposed to conditions simulating the hydrochlorination step and the dissolution step.

TABLE 4. THE CORROSIVE ACTION OF VARIOUS GASES ON
75A TITANIUM IN 6 M HCl SYSTEM

Boiling Solutions, 6-Hr Exposures

Gas Composition	Corrosion Rate, mils per month		
	Vapor Phase, Gas Bubbling Through Solution	Liquid Phase, Gas Bubbling Through Solution	Vapor Phase, Gas Passing Through Vapor Above Solution
None	546.	1063.	--
	458.	1046.	--
N ₂ O	446.	1155.	673.
	373.	1156.	644.
NO	426.	986.	584.
	372.	1017.	537.
NO ₂	0.1	5.5	0.0
	0.5	5.2	Gain ^(a)
NOCl	286.	1024.	Gain ^(b)
	320.	1002.	948. ^(b)
Chlorine	Gain	1124.	Gain
	Gain	1122.	Gain

(a) Gain indicates a gain in weight of 1.3 mg or less on a 1 by 2-in. specimen.

(b) On a repeat run with two replicates, values of 0.2 mil per month, and a weight gain, respectively, were obtained.

		EXPOSURE TIME 162 HOURS				
		TYPE S-816	316 SS	304L SS	ROLLED HAYNES 21	CARPENTER 20
VAPOR
	MIL/MO	2.5	1.5	1.0	1.0	0.4
INTERFACE					DISSOLVED
	MIL/MO	28.3	36.1	48.7	> 80.0	8.1
LIQUID				DISSOLVED	DISSOLVED
	MIL/MO	31.4	36.5	> 76.7	> 88.0	10.4

N40642

FIGURE 7. ZIRCEX ELIMINATION TESTS IN BOILING 0.4 M UCl_3 AQUEOUS SOLUTIONS

In addition to the specimens which were exposed to the cyclic conditions, tensile specimens and corrosion specimens were exposed to the hot step only.

Preliminary tests showed that titanium and tantalum were unsatisfactory materials for construction of the hydrochlorinator because of excessive corrosion rates in the HCl-hydrogen phase at high temperatures. Accordingly, the cyclic tests were confined to alloys high in chromium, cobalt, nickel, etc. The following materials have been investigated in the two-step cycle: Type S-816, Type S-590, Haynes 21, 23, 25, 30, and 36 alloys, Carpenter 20 and Carpenter 20 stabilized, and Type 304 ELC stainless steel. Inconel, Illium R, Hastelloys B and C, and nickel, and those metals listed above, were exposed to just the hydrochlorination step.

A typical cycle consisted of inserting the specimens in a large tube furnace late in the evening. The furnace was flushed with argon and a mixture of hydrogen chloride and hydrogen was passed through. The heaters turned on automatically and heated the specimens to 600 C. Meanwhile, a small piece of zirconium that was inserted with each cycle was held at a temperature so that it would provide ZrCl_4 in the furnace. After 11 hr of this exposure, the HCl and hydrogen were shut off, the furnace thoroughly flushed with argon, and then allowed to cool with the specimens held in an argon atmosphere. The specimens were removed, rinsed in solutions of 3.0, 5.0, or 15.0 M HNO_3 , and then placed in reflux units containing similar acid solutions to which an addition of uranium and chloride had been made. The specimens were exposed to the refluxing solutions for 2 hr, removed, rinsed with tap and distilled water, and quickly air dried. Following this, they were either returned to the furnace for another cycle or, if it were the conclusion of a multiple of five cycles, the specimens were weighed and corrosion rates, expressed as penetration in mils per 100 cycles, were calculated from the weight losses measured. The unit, mils per 100 cycles, is an arbitrary measure which is estimated to be about four times as great as the familiar mils per month unit.

The results of the corrosion rates measured for all of the liquid-phase specimens for the first 20 cycles are shown in Figures 8, 9, 10, and 11.

Only two materials, Haynes 25 and Type S-816 alloys, showed good resistance in the two-step cyclic tests as measured by weight-loss data. These two materials consistently gave corrosion rates of 2 mils per 100 cycles, or less, even after 75 cycles from the high-temperature HCl-hydrogen- ZrCl_4 atmosphere, to solutions which were either 3 M HNO_3 , 0.4 M UCl_3 , or 5 M HNO_3 , 0.01 M UCl_3 . Cycling specimens of these alloys into 15 M HNO_3 with 0.01 M UCl_3 , added at the start of each boiling period, resulted in much higher rates which gradually increased to values around 15 mils per 100 cycles after 75 cycles. These results are shown in Figures 12, 13, 14, and 15.

Metallographic sectioning and inspection of the specimens of Haynes 25 and Type S-816 exposed for 35, 50, and 75 cycles revealed that the specimens which were cycled into the boiling acid solutions underwent severe scaling and an intergranular-type of attack. Corrosion rates based on measurements of the thickness of the unattacked metal are several times greater than those calculated from weight-loss data in the 3 and 5 M HNO_3 solutions. Some of these rates are shown in the form of bars on Figures 12, 13, 14, and 15. Based on these values, Type S-816 alloys could not be recommended for the construction of a Zircex single-vessel hydrochlorinator dissolver.

FIGURE 8. ZIRCEX CYCLIC TEST CORROSION RATES IN 3 M HNO_3 , 0.4 M UCl_3 (SUB-MERGED SPECIMENS ONLY)

FIGURE 9. ZIRCEX CYCLIC TEST CORROSION RATES IN 5 M HNO_3 , 0.01 M UCl_3 , (SUB-MERGED SPECIMENS ONLY)

FIGURE 10. ZIRCEX CYCLIC TEST CORROSION RATES IN 5 M HNO_3 , 0.4 M UCl_3
(SUBMERGED SPECIMENS ONLY)

FIGURE 11. ZIRCEX CYCLIC TEST CORROSION RATES IN 15 M HNO_3 , 0.01 M UCl_3
(SUBMERGED SPECIMENS ONLY)

FIGURE 12. ZIRCEX CYCLIC TEST CORROSION RATES IN 3 M HNO_3 , 0.4 M UCl_3

Corrosion rates determined by metallographic methods are represented by bars.

FIGURE 13. ZIRCEX CYCLIC TEST CORROSION RATES IN 5 M HNO_3 , 0.01 M UCl_3

Corrosion rates determined by metallographic methods are represented by bars.

FIGURE 14. ZIRCEX CYCLIC TEST CORROSION RATES IN 5 M HNO_3 , 0.4 M UCl_3

Corrosion rates determined by metallographic methods are represented by bars.

FIGURE 15. ZIRCEX CYCLIC TEST CORROSION RATES IN 15 M HNO_3 , 0.01 M UCl_3

Corrosion rates determined by metallographic methods are represented by bars.

Apparently, the occurrence of the intergranular type of attack is related to the concentration of chloride. The severity of attack, in the case of Type S-816 specimens, is several times greater in the 5 M HNO_3 solution containing 0.4 M UCl_3 than in the solution of similar HNO_3 concentration containing only 0.01 M UCl_3 . The difference is hardly noticeable with Haynes 25 specimens. The corrosion rates appear to be essentially the same at 35 cycles as at 75 cycles.

If one were to design a hydrochlorinator dissolver of sufficient thickness to withstand corrosion in the neighborhood of 3 mils per month, then the use of Haynes 25 might be considered but, at best, its use would entail calculated risks of the type which would not seem desirable in remotely controlled processes.

Inconel, Haynes 25, Types S-816, Illium R, nickel, and Hastelloys B and C showed good resistance, on the basis of weight-change data, to the hot step (see Table 5). Tensile specimens were exposed to the hot step and portions were also given bend and hardness tests. A comparison of the properties of these specimens with those of others in the as-received condition or after exposure to argon at the same temperature, 600 C, showed that Inconel, Haynes 25, Type S-816, and Illium R were not affected by the hydrochlorinator. Hastelloy C increased in tensile strength and hardness and decreased in elongation. Hastelloy B and nickel were not tested. These results are summarized in Table 6.

It thus appears that several materials are available for the two-vessel hydrochlorination process. The optimum materials of construction for the dissolver in such a process would appear to be titanium or tantalum.

Liquid-Phase Hydrochlorination

Limited studies have been made of the corrosion produced by the liquid-phase Zircex hydrochlorination. Equipment was constructed which enabled specimens to be exposed both above the surface of and submerged in the refluxing double salt $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$. The temperature was held at 425 C while gaseous hydrogen chloride was passed over the surface of the salt at a low rate. Exit bubblers were used to prevent any back diffusion of air and the salt was mixed and stored in an argon atmosphere until the beginning of the test.

Twenty-three metals or alloys were screened as candidate construction materials. The results from these 24-hr tests are shown in Table 7.

In most cases, the corrosion rate is much higher for the specimen submerged in the liquid than for that one exposed to the vapor. Gold, molybdenum, platinum, and tungsten appear to be quite resistant, but drawbacks would be encountered with each of these with regard to designing a hydrochlorination vessel. Molybdenum would seem the best choice of these, but welding techniques with this metal are not sufficiently advanced to allow fabrication of a vessel without difficulty.

TABLE 5. RESULTS OF ZIRCEX CYCLIC TESTS

Hot Cycle Only

Specimen	Corrosion Rate, mils per 100 cycles			
	10 Cycles	30 Cycles	40 Cycles	60 Cycles
Haynes 21	3.85	2.79	Discontinued	--
Haynes 23	1.65	1.94	--	--
Haynes 25	0.24	g(13)	g(20)	0.00
Haynes 30	g(13)	0.24	--	--
Haynes 36	0.13	0.01	--	--
Type S-590	0.75	0.63	0.48	0.37
Type S-816	0.27	g(22)	g(26)	g(33)
Carpenter 20	7.57	6.75	Discontinued	--
Carpenter 20 stabilized	7.69	8.25	Discontinued	--
Type 304 ELC	24.65	20.99	Discontinued	--
Inconel	g(9)	g(41)	g(50)	g(53)
Illium R	g(5)	g(29)	g(26)	g(37)
Hastelloy B	g(3)	g(90)	g(103)	g(142)
Hastelloy C	g(4)	g(45)	g(47)	g(55)
Nickel	g(16)	g(81)	g(87)	g(89)

Note: g indicates a gain in weight, of the number of milligrams shown in parentheses, for 1 by 2-in. specimens.

TABLE 6. THE EFFECT OF HYDROCHLORINATION ON THE MECHANICAL PROPERTIES OF VARIOUS MATERIALS

Exposure Conditions(a)		Tensile Strength, psi		Elongation, per cent	Rockwell Hardness		Radius to Crack in Bend Test, 64th in.
Medium	Time, hr	0.2 Per Cent Offset Yield	Ultimate		B	C	
Type S-816							
As received	--	72,000	145,800	44.9	99		None(b)
As received	--	69,100	143,400	36.6	98.5	--	--
Argon	110	74,500	140,600	28.7	99-100	--	None
Argon	330	71,500	140,000	33.8	--	23-24	None
Hydrochlorinator	110	77,800	151,100	33.0	99.5	--	None
Hydrochlorinator	330	70,700	131,100	26.0	--	19	None
Haynes 25							
As received	--	79,500	157,000	52.8	102-104	--	None
Argon	110	87,800	141,200	23.8	103-104	30-31	None
Argon	110	89,100	146,700	27.0	103-105	30-32	
Argon	330	92,500	130,700	26.0	--	29-30	None
Hydrochlorinator	110	90,900	150,500	30.7	--	28-29	None
Hydrochlorinator	330	91,200	151,000	36.8	105-106	29	None
Inconel							
As received	--	34,300	92,700	42.5	74	--	None
As received	--	34,100	92,900	44.3	74.5	--	--
Argon	110	34,400	92,300	42.7	86	--	--
Argon	110	33,600	91,800	42.5	85	--	None
Argon	330	33,000	90,700	41.2	80	--	None
Hydrochlorinator	110	34,100	91,800	44.0	74.5	--	None
Hydrochlorinator	330	36,700	90,800	43.4	80	--	None
Hastelloy C							
As received	--	54,400	120,000	53.9	91-92	--	None
As received	--	54,500	121,000	54.0	91-92	--	--
Argon	110	56,300	121,000	50.6	93-94	--	None
Argon	110	56,500	120,900	46.8	98-101	18-22	--
Argon	330	57,800	121,000	41.8	--	18	None
Hydrochlorinator	110	85,500	138,100	19.2	--	16-18	None
Illium R							
As received	--	60,000	122,500	38.6	91-92	--	None
Argon	110	67,000	126,000	35.8	97	--	None
Argon	110	65,000	126,000	36.5	96	--	--
Argon	330	62,300	122,200	35.2	--	18-19	None
Hydrochlorinator	110	63,100	119,300	23.2	--	19	None
Hydrochlorinator	330	63,600	123,000	35.2	99	18-19	1
Carpenter 20							
As received	--	51,800	94,300	37.3	--	13	None
As received	--	51,700	94,400	36.0	--	12	--
Argon	110	55,900	97,900	35.1	88-90	--	None
Argon	330	54,900	97,400	35.7	--	12-13	--
Hydrochlorinator	110	54,500	96,100	35.3	--	14	None
Hydrochlorinator	330	53,200	84,000	32.7	84	--	None
Hydrochlorinator	330	53,600	92,400	33.7	83	--	--

TABLE 6. (Continued)

Exposure Conditions ^(a)		Tensile Strength, psi		Elongation, per cent	Rockwell Hardness		Radius to Crack in Bend Test, 64th in.
Medium	Time, hr	0.2 Per Cent Offset Yield	Ultimate		B	C	
<u>Type 304 ELC</u>							
As received	--	30,100	83,600	72.7	70	--	None
As received	--	30,000	82,600	70.3	65	--	--
Argon	110	30,600	83,400	70.0	70	--	--
Argon	110	28,300	83,800	72.5	68	--	None
Argon	330	30,600	84,800	71.8	76-77	--	--
Hydrochlorinator	110	23,700	68,400	67.6	60	--	4
Hydrochlorinator	330	20,500	58,400	52.0	54	--	2
<u>Haynes 21</u>							
As received	--	206,700	233,300	7.3	--	50	--
As received	--	184,700	215,100	8.9	--	48	8
Hydrochlorinator	110	188,800	213,800	0.8	--	48	48
Hydrochlorinator	330	188,300	202,100	1.0	--	46	96
<u>Haynes 36</u>							
As received	--	173,000	217,000	3.5	--	46-50	12
Argon	110	Broke in grip	--	--	--	49-51	96
Hydrochlorinator	110	203,800	228,200	1.9	--	50-51	--
<u>Haynes 30</u>							
As received	--	177,000	207,000	7.4	--	48-49	16
Argon	110	173,000	225,000	2.8	--	47-49	32
Argon	330	179,900	192,700	0.7	--	48-50	--
Hydrochlorinator	110	181,200	191,100	3.0	--	47-48	--
<u>Haynes 23</u>							
As received	--	148,000	200,000	10.4	--	44-47	24
Argon	110	164,000	202,000	3.1	--	49-50	48
Argon	330	158,000	201,100	3.1	--	49-50	--
Hydrochlorinator	110	162,000	198,500	4.8	--	46-47	--

(a) Exposure in argon and in hydrochlorinator was at 600 C.

(b) No cracks at "sharp" bend radius which is less than 1/64th in.

TABLE 7. RESULTS OF ZIRCEX LIQUID-PHASE HYDRO-
CHLORINATION ELIMINATION TESTS

Corrosion Rates of Materials in Boiling
 $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$ + Gaseous HCl , Based on
 24 Hr of Exposure at 425 C

Specimen	Corrosion Rate, mils per month	
	Liquid Phase	Vapor Phase
Platinum	0.00	0.00
Gold	0.01	0.01
Tungsten	0.1	0.3
Molybdenum	0.6(a)	0.4
	--	0.7
Nickel	6.4	0.2
Hastelloy X	8.2	0.5
Hastelloy C	8.2(a)	0.9
	12.2	1.6
	13.0(a)	1.3
Hastelloy C stabilized	10.2	1.0
Inconel X	10.4	0.2
Illium R	10.5	0.7
Hastelloy B	11.4	2.0
Monel	11.9	0.9
Type S-590	13.6	0.7
Inconel	14.0	0.1
Hastelloy F	16.1	0.6
Type S-816	16.5	0.2
Carpenter 20 stabilized	17.6	0.7
Hastelloy W	18.2	2.4
Haynes 36	40.2(a)	4.2
Haynes 25	43.9	0.9
Haynes 30	50.6	0.2
Haynes 23	66.5	2.4
Haynes 21	82.9	3.8

(a) Gas bubbled through melt until plugging occurred.

Molybdenum, nickel, Hastelloy X, and Hastelloy C specimens were also exposed for 7 days in the above environment. The corrosion rates with all but Hastelloy C are considerably lower than those measured during the 24-hr test. Nichrome V specimens were exposed only in a 7-day test.

Specimen	Corrosion Rate, mils per month	
	Liquid Phase	Vapor Phase
Molybdenum	0.04	0.02
Nickel	1.19	0.08
Hastelloy X	2.73	0.07
Hastelloy C	8.39	1.59
Nichrome V	6.24	0.13

Metallographic examination of these specimens following the test revealed that nickel and Hastelloy X had undergone a very slight intergranular penetration at the surface. Similar attack was not observed on molybdenum or Hastelloy C. Nichrome V has not been sectioned for metallographic examination.

Because of the indication of a leveling off in corrosion rates after relatively high initial rates, it is believed that nickel and some of the nickel-chromium alloys might be worthy of a more extensive evaluation.

THE DAREX PROCESS

Fuel elements containing stainless steel as a diluent or cladding may be treated by the Darex process. Here the element will first be dissolved in a mixture of hydrochloric and nitric acids referred to as dilute aqua regia. The chlorides will be stripped from this solution with concentrated nitric acid. Following proper adjustment of the nitric acid solution, uranium will be recovered by the usual methods of solvent extraction.

Elimination-Type Tests

Simple reflux boiling tests of an elimination type were run using solutions which imitated possible Darex solutions at various stages of the dissolution. These Darex solutions were designated as beginning, middle, and final according to their compositions. These are listed at the bottom of Figures 16, 17, and 18.

Some of the tests were made in the presence of 50 or 100 ppm ruthenium. This was added to represent one of the possible fission products which have been reported by ORNL to promote corrosion in other systems. Actually, in the case of these particular solutions, the presence of ruthenium produced no deleterious effects corrosionwise and may have been beneficial in some instances.

The results from the various tests are shown in Figures 16, 17, and 18. The figures show the appearance of the sample at the conclusion of the test, along with the corrosion rates and exposure times. The beginning solution was the most corrosive of the three. This probably results from both the higher acid concentration and the absence of uranium and other metal ions which may, at times, act as corrosion inhibitors. In this solution, the order of merit was from tantalum, which was unattacked, through titanium, Haynes 21, and zirconium, to Type S-816 which showed rates up to 6 mils per month.

FIGURE 16. SPECIMENS FOLLOWING EXPOSURE IN BOILING SOLUTIONS SIMULATING BEGINNING CONCENTRATIONS IN THE DAREX DISSOLVER

N40644

FIGURE 17. SPECIMENS FOLLOWING EXPOSURE IN BOILING SOLUTIONS SIMULATING MIDDLE CONCENTRATIONS IN THE DAREX DISSOLVER

SOLUTION COMPOSITION: 1.0M H^+ , 1.78M Cl^- , 4.46M NO_3^- , 1.10M Fe^{+3} , 0.30M Cr^{+3} , 0.12M Ni^{+2} , 0.40M U^{+6} . DUPLICATE SPECIMENS.

N40643

FIGURE 18. SPECIMENS FOLLOWING EXPOSURE IN BOILING SOLUTIONS SIMULATING FINAL CONCENTRATIONS IN THE DAREX DISSOLVER

In the middle and final compositions, the Haynes 21 and Type S-816 specimens showed rates varying from about 0.1 to 1.5 mils per month. Tantalum, titanium, and zirconium were virtually unattacked. Zircaloy 2 and the titanium-6 w/o aluminum-4 w/o vanadium alloy were also tested in solutions representing final concentrations and were found to be resistant.

All of the titanium and tantalum specimens shown in Figures 16, 17, and 18 were given bend tests. None showed any indication of embrittlement.

Prior to starting experiments with titanium, personnel at various laboratories working with the problem of pyrophoric reactions between titanium and fuming nitric acid were questioned concerning the possibility of similar reactions with Darex solutions. The consensus was that such reactions would not be expected in systems containing as much water as is present in the Darex cycles. Nothing occurred during the studies to alter this opinion.

Corrosion Tests in Operating Dissolvers

In practice, the dissolution process could be operated either batchwise or on a continuous schedule. Both operations have been simulated in corrosion tests. In flowing dissolver tests, a fresh solution of 2 M HCl, 5 M HNO₃ was constantly fed to a Pyrex-glass reaction vessel. The solution was heated externally to maintain it at boiling and a rod of stainless steel (5/16 in. in diameter) was continually fed by gravity through a closed tube so that only a small portion was contacted by the liquid. Dissolution of this rod was reasonably uniform once the temperature became sufficiently high to prevent the stainless from going "passive". The rod dissolved (approximately 1 in. per hr) in such a manner that it formed a conical, very sharply pointed tip. The overflow from this flask was adjusted to give enough retention time within the flask to make as good use of the acid values of the entering stream as possible, without allowing the stainless to become passive.

The other apparatus was constructed in much the same manner, except no inlet and overflow tubes were provided. A charge of fresh acid was introduced into the flask and dissolution of the stainless was continued until no more would dissolve at boiling solution temperatures. This was known as the batch dissolver.

Metal specimens were positioned at the interface between the liquid and vapor, in the vapor phase, both near the solution and high up in the condenser, and a few were totally immersed. In the case of the batch dissolver, a Soxhlet extraction tube was interposed between the flask and the condenser and specimens were exposed to alternate immersion in the condensed vapors in the extraction tube. Also, in both dissolvers, a circular piece of titanium was positioned directly under and in contact with the point of the stainless rod to see if hydrogen absorption by the titanium would occur from the galvanic cell set up between these two dissimilar metals.

The corrosion data gathered from operating the dissolvers for about 3 months, or longer, are given in Table 8. It can be seen that titanium (75A) and tantalum were virtually unattacked. A thin blue-gray coating was formed on the titanium specimens. The titanium-6 w/o aluminum-4 w/o vanadium alloy was somewhat less resistant.

TABLE 8. CORROSION RATES OF METALS EXPOSED TO ACTIVE DAREX SYSTEMS

Specimen Material	Specimen Location	Corrosion Rate, mils per month	
		Batch Dissolver	Flowing Dissolver
Titanium (75A)	Vapor	<u>1839 Hr</u> 0.01-0.07	<u>2483 Hr</u> 0.02-0.03
	Interface	Gain	Gain
	Soxhlet	0.03	--
Tantalum	Vapor	0.01	0.00
	Interface	--	Gain
Haynes 21	Vapor	0.24-0.43	<u>2207 Hr</u> 0.09
	Interface	--	0.38
	Liquid	0.35	--
Type S-816	Vapor	0.52-0.69	--
	Interface	0.73	--
	Liquid	0.81	--
Ti-6 w/o Al-4 w/o V	Vapor	--	<u>1000 Hr</u> 0.15-0.19
	Interface	--	Gain
Crystal-bar zirconium	Vapor	--	<u>45 Hr</u> 67-69
	Interface	--	59-68

Note: Gain indicates a gain in weight of 100 mg or less on a 1 by 2-in. specimen.

Haynes 21 and Type S-816 showed corrosion rates of less than 1 mil per month. Crystal-bar zirconium was severely attacked and pitted under these conditions. This attack, which occurs in the presence of the gaseous decomposition products resulting from the actual dissolution of stainless steel, is certainly different from that occurring in the elimination tests where the temperatures, acid-strengths, and corrosion products are similar, but the gaseous decomposition products are absent.

In this connection, gas samples were taken during one run of the batch dissolver for analysis by the mass spectrograph. They showed that, after 1 hr, appreciable quantities of the gases HCl, chlorine, NO₂, and N₂O were present. HNO₃ was undoubtedly also present.

Specimens of titanium (75A) were removed at intervals during exposure and were analyzed for hydrogen by hot extraction. They were also tested for embrittlement by bending over known radii of decreasing size until cracking was observed. No hydrogen absorption nor embrittlement, as a result of exposure, could be detected.

Titanium specimens containing spot and fusion (inert gas chamber) weldments were also exposed in these systems for approximately 2 months. No deleterious effects attributable to the corrosive environment could be detected. Further work is planned in the flowing dissolver using specimens representing field-service welds. Stressed specimens will also be evaluated.

The titanium disks referred to above were not embrittled and appeared sound and unattacked at the conclusion of the tests. No hydrogen pickup was found by analysis.

A hard sludge or scale formed on the walls of the flask and on the titanium disk supporting the stainless steel rod. An X-ray analysis showed this material to be largely amorphous in character with small amounts of spinels and metallic silicon. This deposit may prove to be objectionable in plant operation of such equipment. The development of means of removal of this scale may prove difficult.

Miscellaneous Tests for Galvanic Attack

The preceding sections have indicated that both tantalum and titanium show the greatest promise as materials of construction for processing tanks from the standpoint of resistance to over-all general attack.

In practice, the metallic elements will be in contact with the container walls. The possibility thus exists for galvanic couples to be set up. In the systems under consideration, it would be expected that the fuel-element metals would be anodic with respect to the container walls. The possibility thus exists that reduction can occur on the tantalum or titanium surface and that hydrogen could be evolved. It is known that hydrogen has deleterious effects on both the metals in question.

An experimental program was undertaken to measure the potentials, half-cell potentials, and cell currents in different systems and to evaluate the possible harmful aspects of galvanic attack.

The polarization curves for tantalum coupled to uranium or Type 304 stainless steel were determined in boiling 2 M HCl, 5 M HNO₃. Figure 19 shows these data. It can be seen that negligible polarization occurred on the stainless steel or uranium, while a considerable drop in potential occurred in the tantalum. The diagram shows that the tantalum-stainless open-circuit cell potential was 1.14 volts and the tantalum-uranium open-circuit cell potential was 1.61 volts. Gas evolution occurred on the tantalum electrode when it was coupled to uranium. None was detected when it was coupled to stainless steel.

Similar measurements were made for the system titanium-uranium-stainless steel. Figure 20 shows that considerably different polarization curves were obtained than for tantalum. First, it can be seen that all three electrodes polarized appreciably. Secondly, the cell currents were approximately 100 times greater than for tantalum couples. It is believed that this indicates more active dissolution of the anode in this case. It should also be mentioned that gas evolution occurred from the titanium electrode when coupled to either the uranium or stainless steel.

Several experiments were run in an attempt to identify the gas evolved at a titanium electrode while it was coupled to dissolving stainless steel. Analysis by means of a mass spectrograph showed that the major constituent of the gas was nitrogen, the minor constituent was water, and there were traces of hydrogen, HCl, NO₂, and oxygen present. It thus appears that the nitric acid, under these conditions, is reduced principally to nitrogen.

To study the deleterious effects of couples, electrolytic cells were set up with tantalum and titanium electrodes. In each cell, the metal in question was made cathodic by an impressed emf, to that value which it reaches in boiling 2 M HCl, 5 M HNO₃, when in contact with dissolving uranium. Carbon rods were used for the anodes in the cells. The cells were operated continuously. Strips were cut from the electrodes at intervals and analyzed for hydrogen after being given a bend test. There was a noticeable embrittlement of the tantalum after 1500 hr. No appreciable embrittlement was detected in the titanium specimens. The results of the hydrogen analyses were not conclusive. The hydrogen content of the tantalum increased from 180 to 350 ppm in 700 hr and then showed little further increase at 1500 hr. No significant increase in hydrogen content was noted for the titanium. However, scaling was observed on the titanium specimens to an extent corresponding to a metal loss of 1.7 mils per month, computed on the weight loss measured after removing the scale by light abrasion. This is a much higher rate than has been observed during dissolver tests where the dissolution of stainless steel provides less difference in potential.

CHLORIDE-STRIPPER STUDIES

Tantalum and titanium specimens were exposed submerged in and above boiling re-fluxing solutions which were chosen to represent different stages during Zircex and Darex stripping. The starting compositions used for Darex stripping tests were 7.0, 9.0, and 10.6 molar in HNO₃ and contained chromium, iron, nickel, and uranium ions in varying amounts. The solutions used for evaluating materials for Zircex stripping were 9, 11, and 14 molar in HNO₃ and contained 0.4 mole of uranium. HCl gas was bubbled

FIGURE 19. POLARIZATION CURVES FOR TANTALUM, TYPE 304 STAINLESS STEEL, AND URANIUM IN BOILING 2 M HCl, 5 M HNO₃ SOLUTIONS

FIGURE 20. POLARIZATION CURVES FOR 75A TITANIUM, TYPE 304 STAINLESS STEEL, AND URANIUM IN BOILING 2 M HCl, 5 M HNO₃ SOLUTIONS

through the solutions to maintain chloride at all times. The solutions thus varied continuously in composition as a result of nitrate removal. It was found, as shown in Table 9, that titanium was quite resistant to these conditions, provided some nitrate was present to furnish passivation to the titanium. Failure of titanium can occur in a catastrophic manner if passivation is not maintained. Therefore, any contemplated design of stripper or rectifier using titanium should provide enough oxidation to maintain the metal in a passive state. As mentioned previously, the nitrate concentration necessary has not been accurately established, but it is thought to be fairly low.

Tantalum specimens were practically unaffected during the 9 weeks that they were exposed. Welded specimens of titanium were also exposed for several weeks. No selective attack could be detected in the heat-affected areas at, or near, the weldments.

PUREX ACID-EXTRACTION SYSTEM

Both the Zircex and Darex head-end processes depend upon a Purex-type acid-extraction system to reclaim the uranium values from the nitric acid solution which will be adjusted following the chloride-stripping operation. Since the chloride-stripping operation may not always be completely efficient, it is possible that the chlorides which remain might lead to stress-corrosion cracking of the Type 347 stainless steel from which the extraction columns would normally be built.

Aqueous solutions were arbitrarily chosen which were: (1) high in the ions from stainless steel dissolution and low in uranium content, and (2) low in stainless steel and high in uranium. Chloride contaminations were added to these, giving a concentration range from 2 or 3 up to 10,000 ppm. One part of this aqueous phase was mixed with 3 parts, by volume, of an immiscible organic phase consisting of 1 part tributyl phosphate to 2 parts, by volume, purified kerosene. Unstressed specimens of Type 347 stainless steel and specimens stressed both to 90 per cent of the yield strength and in excess of the yield strength in the form of a "U" were submerged in the chloride-bearing aqueous phase. This phase was mixed with the organic phase occasionally by shaking.

After over 6 months of exposure of these specimens at room temperature, 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. Chloride contaminations, under the conditions of this test, do not seem to produce any dangerous attack.

CONCLUSIONS

Zircex Technology

A feasible corrosion-resistant container material for the single-unit Zircex hydrochlorinator-dissolver unit is not apparent at the present stage of development. The best choice is Haynes 25, provided penetration rates of approximately 3 mils per month

TABLE 9. CORROSION RATES MEASURED IN SIMULATED ZIRCEX AND DAREX CHLORIDE-STRIPPER SOLUTIONS^(a)

Specimen	Specimen Position	Solution	Corrosion Rate for Weeks of Exposure Shown, mils per month					
			1	4	9	12	16	19
Tantalum	Vapor	9 M Zircex	0.0	0.0	g	-	-	-
	Interface	9 M Zircex	0.0	g	g	-	-	-
	Liquid	9 M Zircex	0.0	g	g	-	-	-
Titanium	Vapor	9 M Zircex	g	0.1	0.2	0.2	Failed rapidly	
	Interface	9 M Zircex	0.1	0.0	0.1	0.1	Failed rapidly	
	Liquid	9 M Zircex	0.4	0.1	0.2	0.1	Failed rapidly	
Tantalum	Vapor	11 M Zircex	0.0	0.0	0.0	-	-	-
	Interface	11 M Zircex	0.0	0.0	g	-	-	-
	Liquid	11 M Zircex	0.0	g	g	-	-	-
Titanium	Vapor	11 M Zircex	0.0	0.1	0.2	0.2	0.2	0.2
	Interface	11 M Zircex	0.0	0.0	0.0	0.0	0.1	0.0
	Liquid	11 M Zircex	0.1	0.1	0.0	0.0	0.1	0.1
Tantalum	Vapor	14 M Zircex	0.0	0.0	0.0	-	-	-
	Interface	14 M Zircex	0.0	g	g	-	-	-
	Liquid	14 M Zircex	0.0	g	g	-	-	-
Titanium	Vapor	14 M Zircex	0.0	g	0.1	0.1	0.1	0.1
	Interface	14 M Zircex	0.0	0.0	0.0	0.0	0.0	0.0
	Liquid	14 M Zircex	0.0	0.0	g	g	g	0.0
Tantalum	Vapor	7 M Darex	0.0	0.0	0.0	-	-	-
	Interface	7 M Darex	0.0	0.0	0.0	-	-	-
	Liquid	7 M Darex	0.0	g	g	-	-	-
Titanium	Vapor	7 M Darex	0.0	0.0	0.0	0.0	Failed rapidly	
	Interface	7 M Darex	0.0	0.0	0.0	0.0	Failed rapidly	
	Liquid	7 M Darex	0.0	0.0	0.0	0.0	0.0	
Tantalum	Vapor	9 M Darex	0.0	0.0	0.0	-	-	-
	Interface	9 M Darex	0.0	g	g	-	-	-
	Liquid	9 M Darex	g	g	g	-	-	-
Titanium	Vapor	9 M Darex	0.0	0.0	0.0	0.0	0.0	0.1
	Interface	9 M Darex	g	g	g	0.0	0.0	0.0
	Liquid	9 M Darex	0.0	g	g	g	0.0	0.0
Tantalum	Vapor	10.6 M Darex	0.0	0.0	g	-	-	-
	Interface	10.6 M Darex	g	g	0.0	-	-	-
	Liquid	10.6 M Darex	0.0	g	g	-	-	-
Titanium	Vapor	10.6 M Darex	0.0	0.0	0.0	0.0	0.0	0.0
	Interface	10.6 M Darex	0.0	g	0.0	0.0	0.0	0.0
	Liquid	10.6 M Darex	0.0	g	g	0.0	0.0	0.0

Note: g indicates a very small gain in weight of the specimens during the exposure.

(a) HCl gas was bubbled continuously through the boiling solutions whose starting compositions were as follows:

Solution Designation	Starting Molar Composition				
	HNO ₃	UO ₂ (NO ₃) ₂	Fe(NO ₃) ₃	Cr(NO ₃) ₃	Ni(NO ₃) ₂
9 M Zircex	9.0	0.40	-	-	-
11 M Zircex	11.0	0.40	-	-	-
14 M Zircex	14.0	0.40	-	-	-
7 M Darex	7.0	0.40	1.10	0.30	0.12
9 M Darex	9.0	0.40	1.10	0.30	0.12
10.6 M Darex	10.6	0.35	0.97	0.27	0.11

can be tolerated. The second choice is Type S-816, which shows even poorer resistance to corrosion (approximately 10 mils/month). At this time, it appears that the process should be run in two steps. Several materials, such as Inconel, Haynes 25, Type S-816, Illium R, and Hastelloy B, appear promising for construction of the hydrochlorinator. The dissolution of the cold residue could then be carried out by transferring it to a container made from titanium or tantalum.

Only preliminary experiments have been completed in the alternate liquid-phase Zircex hydrochlorination system employing $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$ and gaseous HCl at 425 C. Nickel and certain Hastelloys (such as C and X) appear to be worth further consideration. Gold, molybdenum, platinum, and tungsten, which are less attractive from the standpoint of fabricability, showed even greater resistance to corrosion.

Darex Technology

Based on the laboratory-type investigations reported herein, it appears that several materials of construction would prove feasible from the standpoint of corrosion for the Darex dissolver unit. These, in order of merit, are titanium (75A) with a corrosion rate of less than 0.1 mil per month, Haynes 21 with less than 0.5 mil per month, and Type S-816 with less than 1 mil per month.

The studies have shown possible operating problems in the process from scale formation and from charges going passive.

The stripping columns and rectifier could be made from either tantalum or titanium, provided proper oxidizing conditions are maintained at the titanium surfaces.

REFERENCE

- (1) Savolainen, J. E., and Blanco, R. E., Chem. Eng. Prog., 53, 78 to 81-F (February, 1957).

PDM:CLP:ELW:FWF/dc