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CORROSION OF MATERIALS OF CONSTRUCTION FOR MULTIPURPOSE HEAD-END EQUIPMENT IN PROPOSED FUEL REPROCESSING SCHEMES*

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ABSTRACT

The necessity for reprocessing a wide variety of experimental nuclear fuels has created interest in the development of multi-purpose processing schemes. The possibility of handling both stainless steel and zirconium fuel types in the same process equipment is particularly attractive. This paper considers in some detail the corrosion problems in multipurpose aqueous head-end processes for these fuel types and compares them briefly with those in certain combustion and fused salt processes.

Dissolution of stainless steel fuels in aqua regia (Darex process) can be combined with dissolution of zirconium fuels in (a) NH_4F-H_2O_2 mixtures which can be contained in high cobalt alloy equipment or (b) carefully controlled nitrate-HF mixtures which appear to be containable in titanium. Alternatively Darex can be combined with a gas-solid combustion process for zirconium and niobium alloys by using a separate reactor (nickel alloy) for the latter and employing common equipment for feed adjustment and solvent extraction. Yet another alternative is to combine sulfuric acid dissolution of stainless steel fuels with NH_4F dissolution of zirconium fuels in a dissolver constructed of Ni-o-nel or similar alloys. Corrosion data for these proposed processes indicate that rates ≤ 3 mils/mo may be attainable in all cases if process conditions can be controlled to the required degree.

Corrosion data are presented for competitive aqueous processes and are compared with those for the fused salt-volatility process. Areas requiring future corrosion work are outlined.

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CORROSION OF MATERIALS OF CONSTRUCTION FOR MULTIPURPOSE HEAD-END EQUIPMENT IN PROPOSED FUEL REPROCESSING SCHEMES

Since the advent of nuclear power there has been a tremendous amount of experimentation with different types of reactor fuels, but until quite recently there has been relatively little emphasis on the resulting problems of fuel reprocessing and waste disposal. When the industry finally settles upon a few of the more efficient fuel types and develops sufficient volumes of these to warrant separate reprocessing plants there may be no further need for multipurpose processing equipment. During the period of experimentation, however, there will continue to be small volumes of experimental fuel types constructed of exotic materials and in all types of geometries. These must be disposed of in some fashion. Unless they are to be canned and buried intact they must be reprocessed in plants designed to handle more than one type of fuel.

The selection of processes and materials of construction for a given plant of this type must obviously be weighted heavily toward the fuel types which will constitute the bulk of its load. Numerous schemes have been devised for reprocessing various fuel types and a number of these are more or less compatible to operation in common equipment. Table 1 lists certain of these schemes which have been developed. Some of these are head-end processes only; others, such as the fluoride and chloride volatility processes and pyrometallurgy include some decontamination and other parts of the recycle scheme.

The HNO_3-HF system (Niflex) will not be considered except as an adjunct to the Darex process. It can be made almost a universal dissolution process by judiciously varying the proportions of fluoride and nitrate, but close control is usually necessary in order to prevent dissolution of container as well as fuel. Corrosion is not the major problem in the electrolytic-HNO_3 process but niobium or tantalum must be used at least for the anode contact. Pyrometallurgical processes likewise have wide potential applicability but will not be discussed in the present paper.

One of the more versatile of the better developed processes is Darex (dilute aqua regia) which can handle stainless steel fuels and most if not all nickel alloy and aluminum fuels. After the fuel is dissolved in dilute HNO_3-HCl (e.g. 2 $\underline{M}$ HCl-5 $\underline{M}$ HNO_3) the chloride is stripped from the solution either by refluxing with nitric acid or by sparging with NO_2 and air.

Table 1. Reprocessing Head End Schemes and Their Capabilities

1.	Darex (HNO_3-HCl)	Stainless Steel, Ni and Al Alloys, U, U-Mo, U-Al, UO_2, UO_2-SS Cores
2.	Chloride Volatility + HNO_3	Zr and Zr Alloy Fuels Including Alloy Cores
3.	Modified Zirflex (NH_4F-H_2O_2)	Zr and Zr Alloys Including Alloy Cores
4.	Sulfex (3.5-6 M H_2SO_4)	Stainless Steel Jacket Removal
5.	HNO_3-HF Combinations	Almost Universal
6.	Electrolytic Dissolution (HNO_3)	Stainless Steel, Fe and Ni Alloys, Zr Jacket Removal, UO_2, U, U-Al, U-Mo Cores
7.	Fluoride Volatility (Fused NaF-LiF + HF, F_2)	Almost Universal Slow on Stainless Steel
8.	Pyrometallurgical Processes	Presumably Universal

Table 2 lists five candidate materials of construction for the Darex dissolver. It will be seen that tantalum is by far the most resistant with titanium second, and that the high cobalt alloys, Haynes 21, Haynes 25, and S-816 are perhaps satisfactory for the dissolver but not for the high concentration acid stripper. Actually the rate of less than 0.9 mil/mo listed for titanium is conservative; in the presence of even small amounts of dissolved stainless steel rates drop off to a few hundredths of a mil/mo as is shown for the continuous dissolver.

Experience with the high cobalt alloys in Darex environments has been somewhat spotty depending apparently upon the past history and the carbon content of the alloy. Thus the figure of 0.25 mil/mo given for Haynes 25 is better than would have been predicted from earlier tests on this alloy. Haynes 21 supplied as a cast alloy and rolled at Battelle performed much more satisfactorily than specimens specially rolled, welded, and heat-treated at the mill. It seems plain that these alloys are more resistant when quenched than when annealed. In any case their use in a Darex scheme would depend upon a low-temperature and/or low acid chloride stripping step. Decreasing the carbon content would doubtless improve their resistance to Darex environments.

Figure 1 shows the results obtained from exposing titanium in two different nitrate-fluoride-chromate solutions during the dissolution of zirconium alloys. It will be noted that after about seven cycles the rate on the specimen exposed in the acid (HBF_4) solution becomes constant at about 1.2 mil/mo. This is an overall rate; the titanium specimen was in the form of a long strip which was about half immersed in the boiling solution. It is extremely important from a corrosion standpoint not to allow the Cr(VI) to become depleted. The titanium then suffers aggressive local attack, particularly near the interface and in heat-affected regions near welds. The dissolution rate of zirconium in this solution amounts to about 0.6-0.7 mil per minute and on Zircaloy-2 is so uniform that specimens often appear to have been polished. Vapor phase rates on titanium were decreased from a maximum of about 6 to 0.06 mils/mo by the presence of 0.27 $\underline{M}$ Zr^{+4} in the dissolvent during 120 hr exposure. It is not expected that one would construct a titanium dissolver with zirconium fuel as its prime feed, but these data show that zirconium fuels can be processed in titanium equipment on an interim basis.

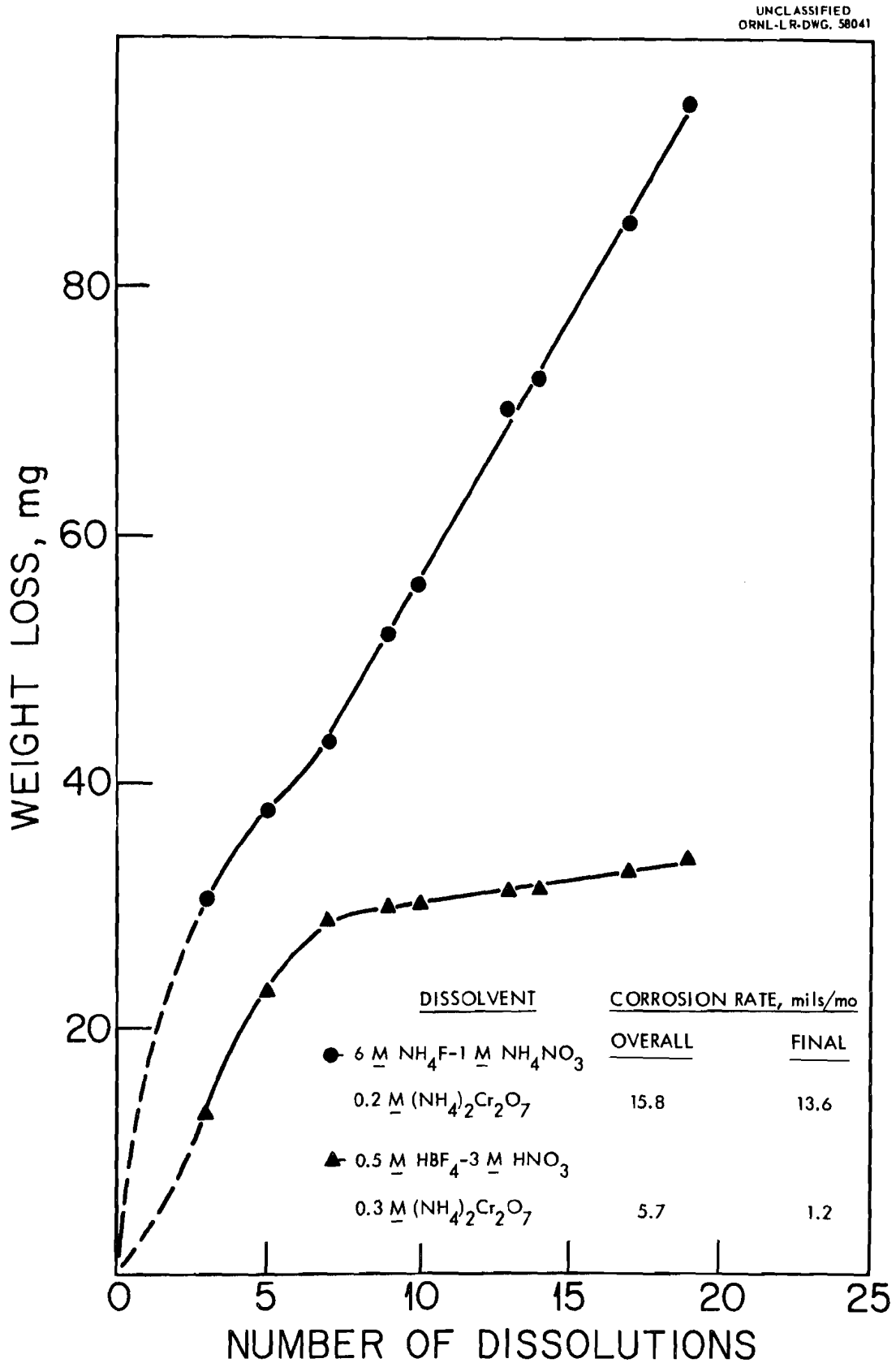

Fig. 1. The corrosion of titanium during cyclic dissolution of Zircaloy-2 in high fluoride solutions.

Table 2. Corrosion in Darex Environments

Metal	Maximum Corrosion Rate, mils/mo			
	Initial Dissolver (250-1300 hr)	Batch Dissolver (1839 hr)	Continuous Dissolver (2000 hr)	Chloride Stripping Column
Titanium	<0.8	0.07	0.03	<0.5
Haynes 25	0.31	-	-	-
Haynes 21	0.77	0.43	0.38	Failed
S-816	6.3	0.81	-	Failed
Tantalum	Neg.	Neg.	Neg.	Neg.

Table 3. Corrosion in Chloride and Oxide Volatility Processes

Environment	Corrosion Rate, mils/mo		
	Haynes 25	INOR-8	Nichrome V
HCl 300°C	0.25	0.3	0.16
600°C	Gain; 2-5	11-16	1.5-5.6
Zircex Cycle (1) $HCl-H_2$ at 600°C; (2) 5 M HNO_3, Boil	3 max	-	-
CCl_4 in N_2, 450°C	2-7	0.2-1.2	0.3-1.1
600°C	1.2-Fail	0.13-Fail	0.7-Fail
Cl_2, 350°C	0.08	0.08	<0.01
600°C	35.2	27.1	8.8
O_2, 725°C	0.02	0.01	0.01

Table 3 lists the corrosion rates observed for various materials of construction in chloride and oxide volatility processes involving reaction between the solid fuel and a gas. In this scheme zirconium and niobium are volatilized as chlorides, carbon (graphite or carbides) as CO, and the uranium "ashes" remaining are dissolved in nitric acid. The HCl system is seen to be one of the easier ones to contain; after seventy-five HCl (600°C)-5 M HNO_3 cycles the maximum rate on Haynes 25 was about 3 mils/mo as determined by metallographic section. Unfortunately it is necessary to alternate the relatively long HCl treatment with a short treatment with CCl_4 to destroy any bulk ZrO_2 on zirconium fuels. This reagent is the most aggressive of any of those listed though the exposure times required are usually relatively short. Chlorine (necessary if the fuel contains niobium) is intermediate between HCl and CCl_4 in corrosivity. Oxygen, even at high temperatures, is easily contained. Fig. 2 shows the strong temperature dependence of Haynes 25 corrosion in CCl_4. Operation with wall temperatures $\leq$500°C should result in corrosion rates $\leq$3 mils/mo.

This system has engineering design difficulties, none of which appear to be insuperable. Fig. 3 shows how conveniently the chloride-volatility process would work in conjunction with a Darex system employing a titanium column for chloride stripping. A large variety of fuels can be reprocessed in such a plant and waste volumes should be much lower than for most competitive processes.

Table 4 summarizes the corrosion rates of Ni-o-nel, Hastelloy F, a related alloy developed for Hanford by Battelle, and Haynes 21 in various Zirflex and Sulfex environments. There is fairly high degree of variation in rates, reflecting the fact that the work was done at at least three sites and that Hanford used special vacuum-melted Hastelloy and ORNL used a special low-carbon variation of Ni-o-nel. In general the lower rates listed refer to these low-carbon alloys. It is obvious that Ni-o-nel is superior to Hastelloy for Sulfex service while for Zirflex Hastelloy F may be slightly superior. The newly developed alloy listed as HW-BMI 20 may be as good or better than Ni-o-nel for combined Sulfex-Zirflex service but performance data are not nearly so abundant at present, and the alloy is not to my knowledge commercially available. It

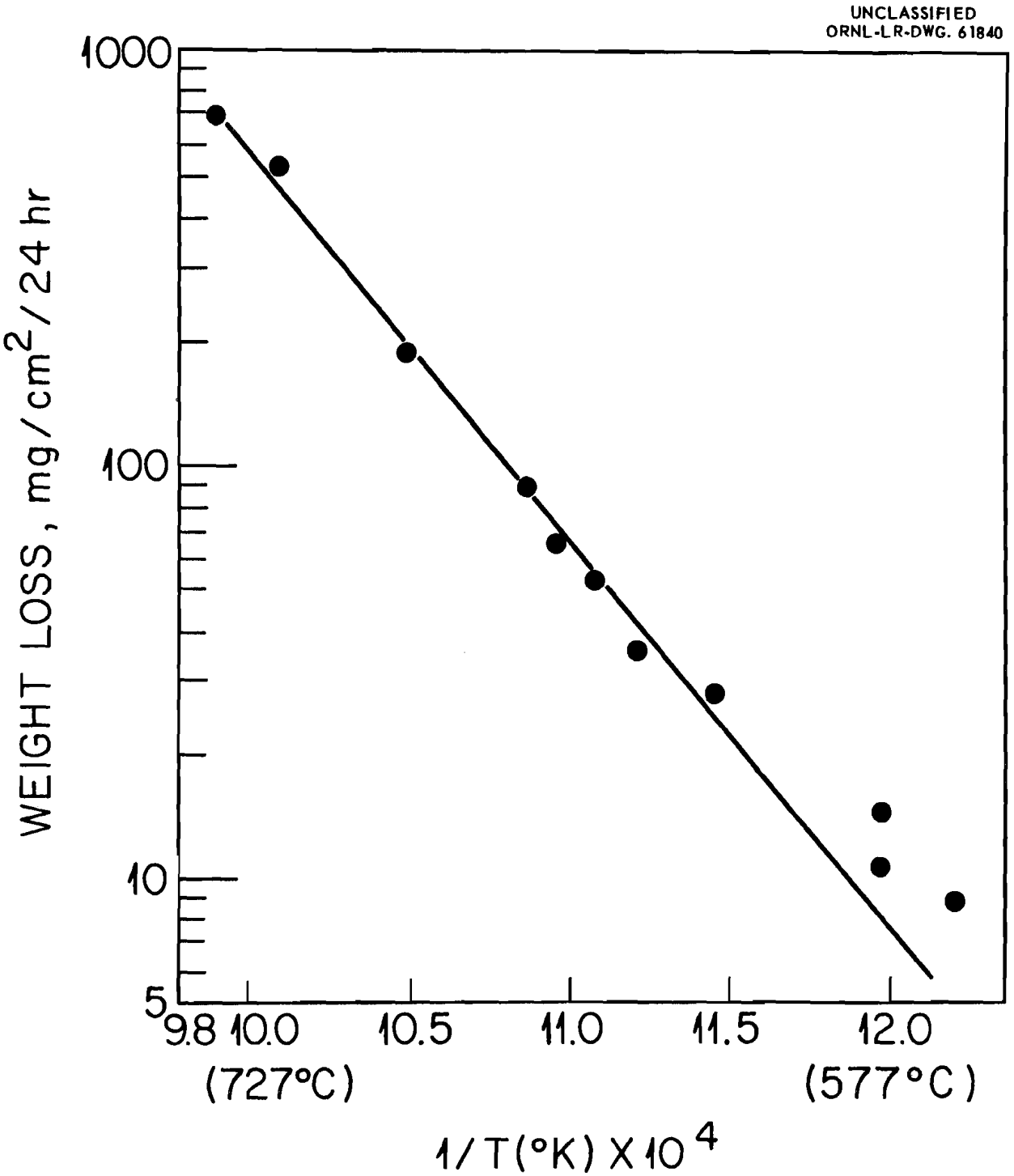

Fig. 2. The temperature dependence of Haynes 25 corrosion in N_2-CCl_4.

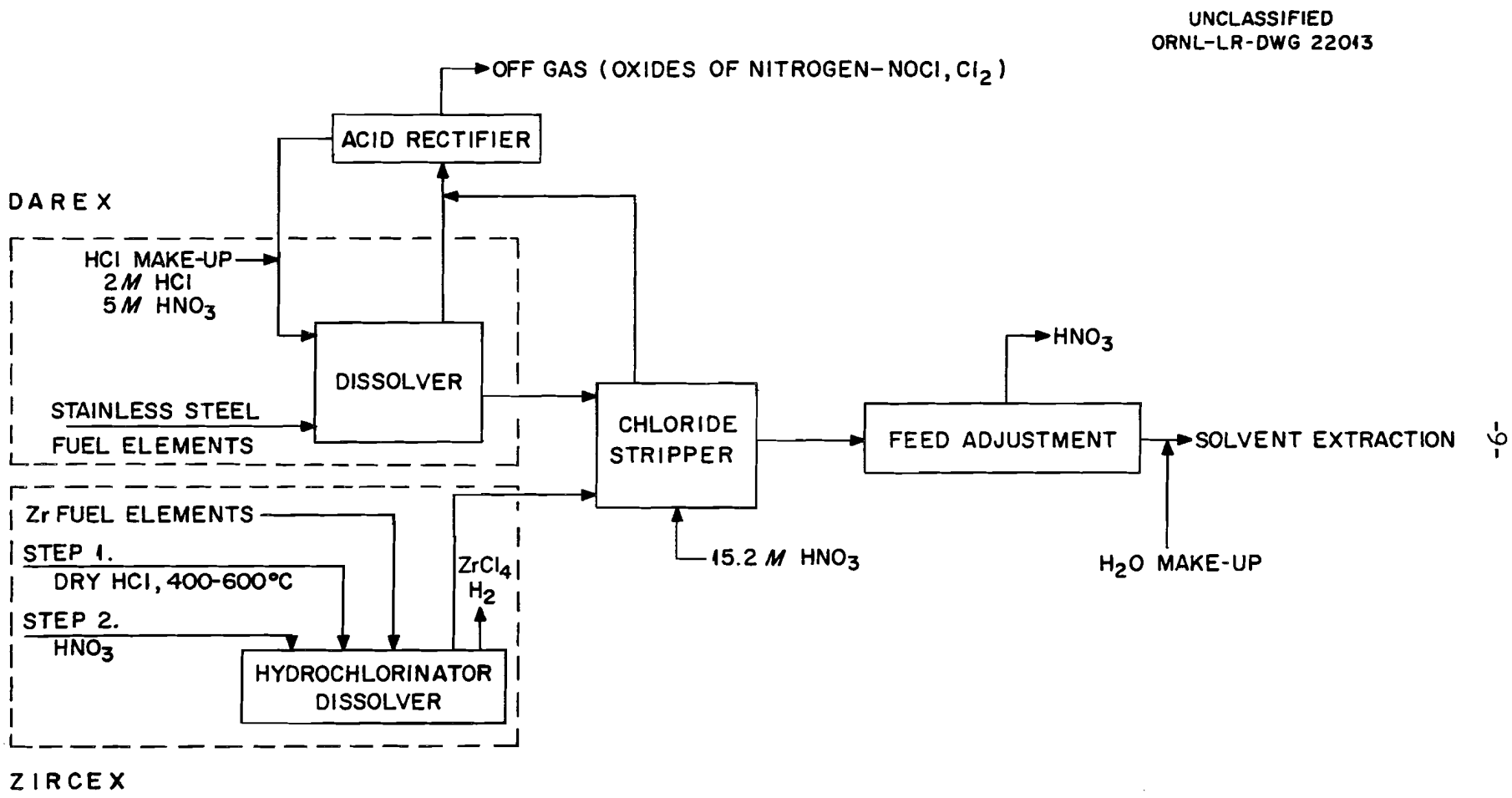

Fig. 3. Schematic flowsheet for combined Darex and Zircex head-end processes.

Table 4. Corrosion in Sulfex and Zirflex Environments

Solution	Corrosion Rate, mils/mo			
	Ni-o-nel	Hastelloy F	BMI-HW Alloy 20	Haynes 21
Zirflex				
6 M NH_4F, 1 M NH_4NO_3	0.8-15	0.15-7.9	0.8-8.4	2.3
Cyclic Declad	4.3-4.8	4.6	-	-
Continuous Declad	2.0-2.4	1.1-1.3	-	-
Modified Zirflex				
5.4 M NH_4F, 0.5 M NH_4NO_3 0.003 M H_2O_2				
Continuous	1.1-1.2	2.7-3.1	-	0.67
Sulfex Declad				
6 M H_2SO_4	7.3-8.3	74	-	275
4 M H_2SO_4	2.1-4.4	18	2.0	-
Spent 4 M	0.7-2.4	29	0.9	-
Cyclic Sulfex-Thorex				
Coupons	1.4-8.5*	-	-	-
Container	2.1-4.9*	-	-	-

*Metallographic Section.

will be observed that the addition of peroxide generally results in a marked increase in corrosion resistance of the candidate metals to Zirflex solutions. Haynes 21 is included in the table to show its resistance to Zirflex solutions. It could conceivably be used as a dissolver material in a combined Darex-Modified Zirflex reprocessing scheme. Carpenter 20, Illium R, and Illium 98 as well as certain other alloys were tested for Sulfex service, but commercial grades were found to be inferior to Ni-o-nel.

Table 5 lists corrosion rates experienced by various alloys in spent dissolver solutions and solvent extraction feed solutions. Hastelloy F ($\leq$0.7 mil/mo) was the most generally satisfactory material tested. Had the free fluoride in the UO_2 dissolvent been complexed with aluminum, titanium would have performed better. Though stainless steels were not extensively tested in this particular series, it is probable that 309 SCb (which was not tested) could be used provided that

1) the chloride from Darex is first stripped down to about 0.01 M,
2) Sulfex effluent is spiked with 0.1 M nitrate or more,
3) the free fluoride in the UO_2 dissolvent is adequately complexed.

The corrosion observed in the Fused Salt-Volatility Process is summarized in Table 6. Based on time employed for gas sparge the corrosion rate for an INOR-8 hydrofluorinator was about 0.05 mil/hr and that for a nickel fluorinator was about 0.9 mil/hr. These are figures from pilot plant operation. In a laboratory scale fluorinator Hymu 80 performance indicated a rate equal to about one-twentieth of that experienced by nickel. A great deal of painstaking work has gone into the corrosion evaluation of this system and further improvements can be expected.

Table 7 lists multipurpose reprocessing schemes which appear possible from data at hand, but which, to my knowledge, have never been utilized. The corrosion rates listed represent estimated ranges and will, of course, vary considerably in each case depending upon which of the processes is used principally and the care which is taken to control processing conditions. The effect on corrosion of switching from one reprocessing scheme to another has not been evaluated.

Table 5. Corrosion in Spent Dissolver and Solvent Extraction Feed Solutions

(330 hr or longer)

Process Solution	Maximum Corrosion Rate, mils/mo				
	304L	Ti	Ni-o-nel	Hastelloy F	Carpenter 20 SCb
Darex					
Spent, 35°C	Failed	0.01	52	0.09	80
Feed, 25°C***	<0.01	Neg.	-	-	-
Thorex					
Spent, 35°C	-	0.01	0.03	0.03	0.03
Zirflex					
Spent, 35°C	-	6.1	0.01	0.05	0.03
Feed	0.1-0.2*				
Sulfex					
Spent, 35°C	-	0.01	0.08	0.01	0.02
UO_2 Core**					
Spent, 35°C	-	0.03-8	0.25	0.69	0.49

*Some localized attack.

**1.5 M U in 10 M HNO_3, F^- contamination up to 0.1 M.

***Solvent extraction feed, Cl^- ≦1% by weight (~0.03 M).

Table 6. Corrosion in Fused Salt-Volatility Environments

Material	Corrosion Rate	
	Laboratory Tests (mils/mo)	Operation (mils/hr)
Hydrofluorinator, HF sparge, 700°C		
INOR-8	19-21	0.06
Hastelloy X	19-89	-
90 W-5 Ni-5 Cu	31-41	-
Fluorinator, F_2, Sparge, 500°C		
INOR-8	0.1-11	
L Nickel	0.1-4	0.9
Hy Mu 80	0.1-2.5	0.05 (?)

Reprocessing cycle is 18 hr in hydrofluorinator, 1.5 hr in fluorinator.

Fused Salt: 27-48% NaF, 52-42% LiF, 0-45% ZrF_4, UF_4.

Table 7. Some Possible Multipurpose Processing Schemes

Process Combination	Materials	Estimated Max. Corrosion Rates (mils/mo); Remarks
1. Darex-Acid Fluoride Cr(VI)	Ti	<0.5 Darex; 2-4 in F^-
2. Darex-Cl Volatility	Ti Haynes 25	<0.5 1-10 depending on cycle
3. Darex (NO_2 Strip) - Mod. Zirflex	Haynes 21 (Poss. Haynes 25, S-816)	<3 Alloy fabrication not well developed
4. Sulfex-Mod. Zirflex	Ni-o-nel	2-5 Low C Alloy Superior

Titanium can be expected to perform admirably in any Darex solution and in addition can be used for processing any fuel for which nitric acid is the dissolvent. For example, graphite fuels can be decomposed in titanium by treatment with 20 M HNO_3 at a corrosion rate equal to or less than 0.1 mil/mo. It can be used for dissolving ThO_2 in 15 M HNO_3-0.04 M F^-; initially rates are as high as 11 mils/mo but the attack is uniform and the rate drops off rapidly to a few tenths or hundredths of a mil/mo as thoria is dissolved. Further work needs to be done on the passivation of titanium in fluorides in the presence of Cr(VI), but enough information is at hand to justify the use of a titanium dissolver on an interim basis for small volumes of zirconium fuels.

Further corrosion testing needs to be done on various candidate materials for the chloride volatility process, particularly on the effect of the gas reaction-nitric acid or water flush cycle. Unfortunately, other priorities have prevented a full effort in solving the engineering design problems in this system.

The third process listed (Darex-Modified Zirflex) is dependent upon a type of alloy which was developed for high temperature strength rather than for resistance to aqueous corrosion. The corrosion resistance can almost certainly be improved by lowering the carbon content and using the alloy in the quenched rather than the annealed condition. This combination is also hampered by the necessity for a low acid or low temperature chloride stripping process which has been shown to work but has not been thoroughly evaluated.

The fourth process, Sulfex-Modified Zirflex, makes use of rather well-known chemical systems as well as a readily available commercial alloy (Ni-o-nel), though for best corrosion results a vacuum-melted, low carbon variation should be specified. This process is not, in my opinion, as versatile as any of the Darex processes and has the further disadvantage of producing two types of waste (sulfate and fluoride) which are difficult to dispose of. Within these limitations, however, it appears to be ready for use with a minimum of developmental work.

Acknowledgment

In addition to the sources listed under "References" much of the data summarized herein was obtained by J. C. Griess, E. S. Snavely, L. Rice, and D. N. Hess of the Corrosion Section, Reactor Chemistry Division, Oak Ridge National Laboratory and has not yet appeared in any topical report. Data for the fused fluoride salt corrosion was obtained from informal Battelle memoranda to R. P. Milford and A. P. Litman of the Oak Ridge National Laboratory. Discussions with representatives of the Haynes-Stellite Division, Union Carbide and Carbon Corporation, the Allegheny-Ludlum Steel Company, and the Battelle Memorial Institute were helpful in evaluating the potential of the cobalt alloys.

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