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ABSTRACT

Laboratory-scale and engineering-scale efforts to recover uranium (and possibly the niobium) from spent Rover fuel elements are reported, and the status of each aspect of the work is presented, including the evaluations.

Basically, the fuel consists of pyrolytic-carbon-coated spheroids of uranium carbide dispersed in a graphite matrix. The coolant channels in the graphite are lined with niobium carbide. For uranium recovery, in essence the fuel element is first oxidized to remove the graphite, leaving an ash that contains principally the oxides of uranium and niobium; then, the uranium is separated from the niobium and nonvolatile fission products by appropriate methods. Most of the chemical problems are associated with the niobium and the pyrolytic carbon coating.

The Combustion-Fluorination Process represents the main effort, and basically it involves the combustion of the fuel and the fluorination of the ash; the uranium is recovered as UF_6. The method is in the pilot-plant stage of development. This issue includes the following information: the status of development, and the material balances, fluorination times and rates, and other pertinent information presented as a summary of the uranium recovery experience to date. In addition, laboratory-support work on problems connected with uranium recovery is also reported. The fabrication, installation, and stress-analysis calculations for the experimental combustion-fluorination reactor are reported. The slab reactor will replace the present cylindrical reactor. Also reported are the details of corrosion tests conducted at Battelle with NbF_5 and L-nickel, Monel, and INOR-8.

Alternatives to combustion-fluorination involve the dissolution of the ash with hydrofluoric-nitric acid mixtures, thereby preparing solutions adaptable to the solvent-extraction separation of the niobium, uranium, and fission products. Several processes are based on this system, and they are: the Deline-Burn-Dissolve, the Burn-Dissolve, and the Burn-Leach Processes. Reported in this issue is a brief account of the progress of a related subject, the paths and fates of the fission products during the combustion step.

Other alternatives to combustion-fluorination include the gaseous chlorination of the combustion ash to form the volatile, separable chlorides of niobium and uranium, and the chlorination of the ash with hot hexachloropropene (HCP) followed by appropriate solvent extraction steps to separate the niobium and uranium. These methods are largely in the laboratory stage of development, but reported in this issue is an account of a "warm-cell" demonstration of the burning and chloride volatility process.

1. INTRODUCTION

1.1 Brief Survey of the Problem and the Research

The studies are being made in order to develop an efficient and economical process for the recovery of uranium from spent Rover fuel, which consists of uranium carbide (coated with pyrolytic carbon) dispersed in graphite, with niobium carbide liners in the coolant channels. The burnup of the elements will be low, and they will not be excessively radioactive. The problems derive principally from the pyrolytic-carbon coating on the uranium carbide spheres and from the niobium carbide liners for the coolant channels.

The coating is very resistant to chemical attack, and a preliminary step in the process necessarily is the removal of the coating, whether or not this step is to be followed by fluorination, chlorination, or aqueous processing. This first step is conveniently done by simple combustion, which also includes the advantage of removing the bulk of the fuel element (the graphite moderator) as carbon dioxide. Then, the ash (oxides of uranium, niobium, and nonvolatile fission products) may be fluorinated, chlorinated, or treated by an aqueous mixture of hydrofluoric and nitric acids in order to recover the uranium. It may even be possible to eliminate hydrofluoric acid, according to a recently introduced variant of the aqueous-processing route. The combustion step, on the other hand, may or may not result in sintered oxides of uranium and niobium, depending on the controllability of the temperature, and dense sinters may make other steps in the recovery more difficult to

take. As stated above, the niobium carbide liners and the pyrolytic carbon coatings on the fuel spheres are presenting the most difficult problems and consequently requiring the most attention, whatever the approach.

The main effort is the Combustion-Fluorination Process, which essentially consists in burning the element in oxygen in order to produce a combustion ash, and then fluorinating the ash in order to separate the uranium (as the volatile hexafluoride) from the fluorides of niobium and the fission products. Some of the fission products are also volatile, as is niobium fluoride, but, due to their physical properties, they can be separated from the uranium by adsorption on beds of sodium fluoride, for example. The Combustion-Fluorination Process is in the pilot-plant stage of development.

The alternative methods for recovering the uranium from the combustion ash are the aqueous nitric-hydrofluoric acid process and the liquid- or gas-phase chlorination processes and their variants. According to the aqueous route, it may be possible to circumvent the sintering of the niobium pentoxide by first dissolving the liners from the elements in order to prevent the appearance of niobium oxide in the combustion ash, thereby improving the process whether the postcombustion steps follow an aqueous or a gaseous route. That development is called the Deline-Burn-Dissolve (DBD) Process and has advanced to the point of a pilot-plant study. Two variations of the DBD Process have also been introduced: the Burn-Dissolve and the Burn-Leach Processes. The Burn-Leach Process, should it be workable, offers the advantage of eliminating hydrofluoric acid from the aqueous processing. Included in this work is a study of the fate of the fission products during the combustion step.

The other alternative to the Combustion-Fluorination Process is one that basically involves the liquid-phase, low-temperature chlorination of the combustion ash with hexachloropropene (HCP), or high-temperature, gas-phase chlorination, plus the useful variants that may develop as the study advances. Liquid- or gas-phase chlorination have so far shown themselves worthy of study because early corrosion results indicate that

the nickel reactor will not be attacked severely. Gas-phase chlorination is very similar in many important respects to the fluorination method, but liquid-phase chlorination with HCP has special advantages. For example, it is run at low temperature (below 200°C), and the product is readily adaptable to extraction by tributyl phosphate--Amsco mixtures. On the other hand, gas-phase chlorination may offer promise as a method not only for separating the uranium in bulk but for purifying it, though this has yet to be demonstrated. The gas-phase work is done in an apparatus called the "Torrefactor." In addition, some work has been done on the demonstration of a flowsheet for the gas-phase chlorination process (combustion of the fuel, followed by gas-phase chlorination at 600°C with 15% CCl_4--Cl_2).

Laboratory work in support of the processes is continuing to help identify and solve problems as they arise.

The status and evaluation section below is confined to the progress made on the work done during this reporting period. The other progress reports in this series are: ORNL-TM-170, 199, 227, 267, 298, 373, 408, 426, 443, 509, 520, and 538.

1.2 Status and Evaluation of the Efforts

Recovery of Uranium from Spent Rover Fuel by the Combustion Fluorination Process. This month's contribution is largely a tabulated summary of the fluorination experience, with material balances, fluorination times and rates, and other useful information being given. The main conclusions derived from the data and observations made during the experiments are:

The system operation during both runs was erratic, as has been reported previously. Some of the loss to the still-bottom residue may be due to these break-in operational difficulties. The quantity of uranium removed by and remaining after distillation was small enough to indicate that a second partial condensation might provide sufficient separation and eliminate the need for distillation.

The uranium recovery obtained indicates a need for more precise weighing and possibly better information on the composition of the fuel. With respect to uranium losses, the uranium on the sodium fluoride bed

operates at 400°C is not really a loss, because it has been shown that this uranium can be completely desorbed by fluorinating the bed at 400°C.

Laboratory Work in Support of the Combustion-Fluorination Process. The main emphasis in the support work was on uranium recovery problems, and two sources of uranium holdup were studied: the V-104 niobium-cleanup trap and the product trap, both consisting of pellets of sodium fluoride and both of which chemisorb UF_6 or NbF_5, depending on the temperature of operation, thereby leading to a separation of the uranium and niobium. The results of the thermogravimetric studies on the removal of uranium (as UF_6) from the traps led to the following conclusion:

Uranium, complexed in any valence state on sodium fluoride, can be recovered with high yields by refluorination and consequent volatilization at temperatures in the range 375 to 475°C. Also, niobium fluorides in no way affect the yield when present in the pellets in niobium/uranium ratios up to 30.

Slab Reactor V102 Mark II. This contribution to the monthly report is a discussion of the following subjects: "Criticality Review Request," "Fabrication," "Installation," and "Stress Analysis Calculations."

NbF_5 Corrosion Results. At Battelle Memorial Institute, corrosion tests with NbF_5 and Monel, INOR-8, and low-carbon nickel showed that any of the three metals would be satisfactory for NbF_5 boiler fabrication, but the most satisfactory would be INOR-8 (approximately 0.2 mil/month corrosion and no intergranular attack or surface roughening).

Aqueous Processes for Recovering Uranium from Rover Fuel Combustion Ash. Equipment for studying the fate of fission products during the burning of Rover fuel in oxygen has been assembled and partially cold-tested. The results of the cold tests indicate that the equipment will be suitable for use in the forthcoming hot-cell experiments with Kiwi-B4A fuel specimens. The hot-cell tests are tentatively scheduled to begin on May 15, 1963.

Chlorination and Chloride Volatility Studies on the Recovery of Uranium from Rover Fuel Combustion Ash. Exploratory experiments were made in a "warm-cell" on the adaptation of a chloride volatility system

to the recovery and decontamination of uranium contained on spent Rover fuel elements. The results of these preliminary tests showed a reasonable separation of niobium from the uranium, but with gross-gamma decontamination factors of only about 2. Ruthenium and zirconium-niobium appeared to be the principal contaminants in the uranium product, while 1 to 2% of the uranium was found in the separated niobium and volatile fission product fraction. Four recommendations are offered with respect to additional laboratory work, prerequisites to the development of a more useful flow-sheet. Two more runs, with higher-irradiated fuel, will be made in order to point out the routes taken by the fission products during the steps on the Chloride Volatility process.

2. RECOVERY OF URANIUM FROM SPENT ROVER FUEL BY THE COMBUSTION-FLUORINATION PROCESS

R. W. Horton
R. S. Lowrie
F. G. Kitts
L. E. McNeese

2.1 Introduction

The fuel being used in reactor designed for the Rover project is a dispersion of enriched uranium carbide in graphite, and the large quantity of uranium required for ground testing justifies uranium recovery. However, the use of protective coatings on the uranium particles, and the use of niobium carbide liners for the propellant gas passages makes the chemical separation of uranium from graphite very difficult when using conventional aqueous methods. Accordingly, new process methods designed especially for this fuel are being developed. At present, the most feasible methods all use combustion with oxygen to eliminate the graphite and convert the metal carbides to oxides. The separation of uranium from other combustion products by aqueous methods and by the fluoride volatility process is being studied.

2.2 Status of Development

The cold-trap portion of the separation system has accomplished about 98% of the separations duty during fluorination, based on two fluorination

runs. The packed-column section was revised to allow more flexible heating and better temperature sensing. Still operation has not been successful to date, largely because of insufficient information on properties of the still-bottom fraction.

2.3 Experimentation

The material balances, fluorination times and rates, and other pertinent information are included in Table 1, which summarizes uranium recovery experience to date.

Table 1. Summary of Fluorination Data from Combustion-Volatility Facility in Building 3503

	Run F-1	Run F-2
U charge, g (from fuel composition)	2572	2142
Total time to fluorinate, min	252	335
Total fluorine used, standard liters	3074	2972
Fluorine rate (g moles/(min)·(ft^2 vessel cross section)	4.0 Avg. 6.2 Max.	2.9 Avg. 6.2 Max.
Fluorine utilization, %	50	43
U recovered on 100°C NaF bed, g	2541 (analysis) 2636 (wt gain)	2137 (analysis) 1952 (wt gain)
U recovered on 400°C NaF bed, g	85	67.5
U recovered by distillation of combined F-1 and F-2 residue, g	31.5	
U left in still residue, fluorination runs F-1 and F-2 combined, g	62	
Total recovery of U, %		
By analysis	103.0	103.2
By weight gain	106.2	94.9

The system operation during both runs was erratic, as has been reported previously. Some of the loss to the still-bottom residue may be due to these break-in operational difficulties. The quantity of uranium removed by and remaining after distillation was small enough to indicate

that a second partial condensation might provide sufficient separation and eliminate the need for distillation.

The uranium recovery shown indicates a need for more precision in weighing and possibly better information on fuel composition. In the recovery table, the uranium adsorbed on the 400°C NaF bed is not considered a loss, since laboratory experiments have shown that this uranium can be completely desorbed by passing a fluorine stream through the bed while it is at 400°C.

3. LABORATORY WORK IN SUPPORT OF THE COMBUSTION-FLUORINATION PROCESS

C. E. Schilling S. Katz G. I. Cathers

3.1 Uranium Holdup

The major emphasis in laboratory support of the Unit Operations' Combustion-Fluorination Processing of Rover fuel has been on uranium recovery problems, and two sources of uranium holdup in the process were studied: (1) the V-104 niobium-cleanup trap (NaF hold at 400°C) and (2) the UF_6-product trap: (NaF held at 100°C). The present study of these two types of materials was done to determine causes and provide a remedy for losses of uranium in each.

3.1.1 V-104, Niobium Cleanup Trap

The variable color of the pellets from this trap indicated differences in composition, and the colors of the pellets fall into three categories: white, yellow, and black, each type of pellet having characteristics that are described briefly below.

The largest fraction was white, as normally expected for NaF-complexed NbF_5. However, these also contained reduced uranium identified by x-ray analysis as Na_3UF_7, with other unidentified lines.

The second largest group, which varied between yellow and greenish-yellow, held uranium compounds not identifiable by x-ray analysis. When dissolved in water it was found that the uranium was present both as UO_2^{2+} and U^{4+}. The former was identified in the solution (yellow), and the

latter remained as a green precipitate, which was washed, dried, and identified by x-ray analysis as β_3-Na_2UF_6(IV).

The third fraction of pellets, black, were often unevenly distributed. Spectrographic analysis showed higher trace amounts of iron and copper in these than in the lighter colored ones, which probably accounts for their black color. These impurities are not believed to have been introduced during manufacture. There seems to be no evidence that the presence of copper or iron impurities in the range 0.001 to 0.01% in any way accounts for uranium holdup. However, the niobium content was found to be highest in these black pellets.

It was concluded that until causes could be established for the existence of lower-valence sodium fluoride complexes of uranium in the cleanup-trap pellets, a better approach to solving the problem of uranium recovery was to determine the conditions necessary for refluorination and volatilization of all uranium species. The recovery of uranium as the hexafluoride should proceed rapidly at 400°C by decomposition of the 3 $NaF \cdot UF_6$ complex.[1]

It was found by thermogravimetric analysis in a fluorine atmosphere that the uranium volatilization from selected yellow pellets containing 5.9% U proceeds very rapidly starting at 375°C and is almost completed at 475°C. Analysis of the thermogravimetric analysis postfluorination residue, which had gone as high at 600°C without further weight change, showed 0.04% U and 1.19% Nb. This corresponds to a uranium revolatilization of 99.4%.

3.1.2 Product-Trap UF_6 Recovery Studies

A two-stage thermogravimetric study similar to the above was made of the product-trap sodium fluoride pellets, all of which had a uniform, deep-yellow color. The first stage was made in a helium-atmosphere to test whether all or only part of the uranium could be removed by heating in an inert atmosphere. The second thermogravimetric analysis was done in fluorine to determine the uranium remaining unrecovered in the first by reason of its existence in lower valence states.

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[1] G. I. Cathers, M. R. Bennett, R. L. Jolley, Ind. Eng. Chem. 50, 1709 (1958).

The total uranium volatilized from a 1208-mg sample in helium was 72 mg, presumed to be UF_6. At this point, the color of the complex was green. The total uranium fluorinated and volatilized in step two was 303 mg. Thus, only about 19.2% could be recovered by using only an inert atmosphere. After recovery of the remaining uranium with fluorine, the color of the pellets was pure white, indicating that very little uranium remained. The presence of NaF and possibly NbF_3 or NbO_2F (both questionable) accounted for all the lines in the x-ray diffraction pattern of the residue.

In summary, it can be stated that uranium, complexed in any valence form on sodium fluoride, can be recovered with high yields by refluorination and volatilization at temperatures in the range 375 to 475°C. It can be further noted that the presence of niobium in no way seems to affect the yield of uranium when present in niobium/uranium ratios up to 30.

4. SLAB REACTOR V102 MARK II

4.1 Criticality Review Request

A criticality review request was prepared and submitted for the experimental oxidation-fluorination slab reactor for the combustion-volatility facility in Building 3503. Approval is requested for a uranium batch limit of ≤10 kg of U^{235} in the 2-1/2-in.-wide, 24-in.-long, 48-in.-high slab vessel. The submission also requested approval of a plant-sized reactor vessel that would have a batch size of ≤20 kg of U^{235}. Double batching would be conceivable in the event of failure of procedural safeguards. The dimensions of the plant-size unit would be approximately 4-1/2 ft long by 5 ft high, with an internal thickness of 2-1/2 in. Limited availability of depleted-uranium dummy fuel for the experimental program may make it desirable to use enriched, unirradiated fuel scrap to complete the process development program. Assuming that appropriate building, equipment, and operating changes will be made, the review committee was also asked if the safety of V102 Mark II was such that it was reasonable to consider using it in Building 3503 if it became necessary to use enriched fuel in the development program. Committee action on the request is expected early in May.

4.2 Fabrication

Shop work was completed on V102 Mark II, and the reactor was delivered to ORGDP on April 18, 1963, to the Engineering Development Department so that a 10-to-15 mil coat of gadolinium-samarium oxide could be plasma-sprayed on the outer surface of the cooling channels.

The reactor is shown on Figs. 1 and 2, which are views of the side and end, respectively. After stress relieving, the inside thickness of the reactor was checked and found to vary between 2-5/16 and 2-1/2 in. Only a small area of the shell had a 2-1/2-in. width. Closer adherence to the specified thickness of 2-7/16 in. $\pm$ 1/16 in. is believed possible had it not been necessary to remove and reweld the first two shell welds because of defects.

4.3 Installation

A study sketch of the proposed temperature-control zoning for V102 Mark II was distributed for comments. The reactor is divided into five heating and cooling zones, and the fuel bed is divided into three zones. The heating and cooling zone height is smaller near the bottom of the reactor so that better temperature control can be obtained as the bed shrinks during oxidation and during fluorination. Sixty temperature-measuring points are required for reaction control, five air and eighteen water supply lines are required for cooling, and 47 kw of electrical heat is provided on the shell.

Isometric drawings are being made of the piping manifolds on the reactor to permit pre-piping the reactor before installation.

4.4 Stress Analysis Calculations

CF Memo 63-4-38, Design Report: Mark II V102 Vessel for Advanced Reactor Fuel Processing, was issued by A. E. Spaller (Engineering and Mechanical Division). Minor dimensional changes were made on the reactor after the calculations reported above were made, and they resulted in a stronger vessel than was originally estimated. A 1/16-in. corrosion allowance is assumed. The revised internal design pressure in the vessel as a function of vessel temperature is as follows:

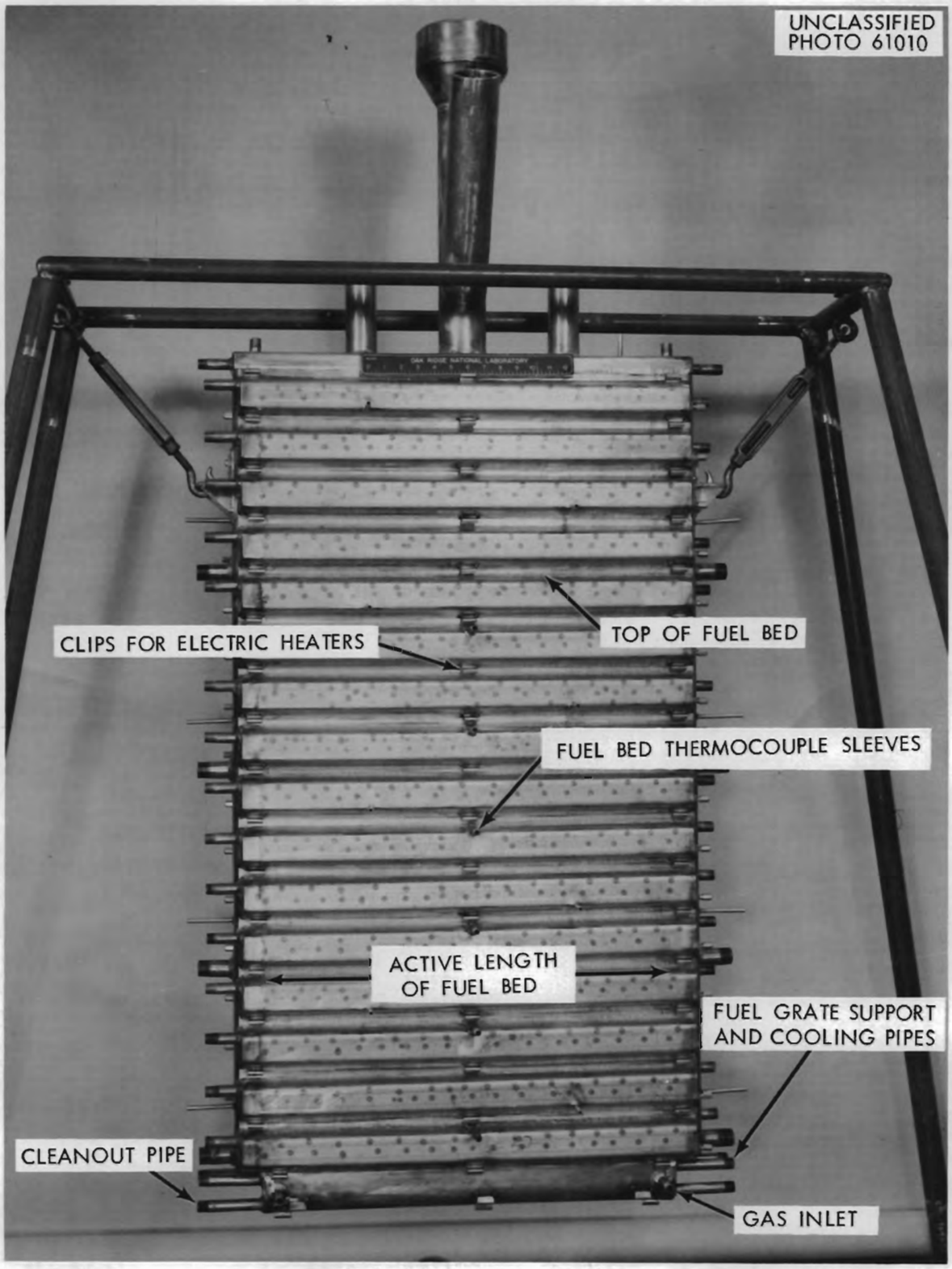

Fig. 1. V102 Mark II Reactor, North Side.

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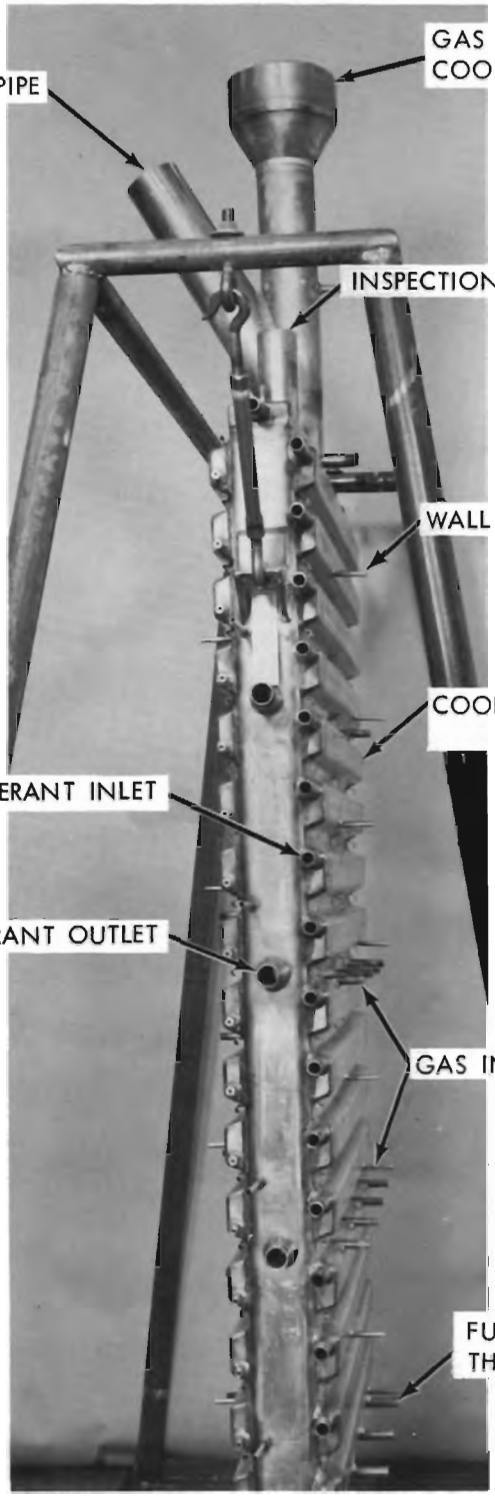

Fig. 2. V102 Mark II Reactor, West End.

Temperature (°F)	Allowable Internal Pressure (psi)
1100	5.6
900	13.4
700	22.1
100	22.4

The report included calculations of the wall stresses under heat transfer conditions with the vessel at 1100°F, 5-psi of internal pressure, and 100°C temperature difference from the inner wall of the vessel to outer wall of the jacket. Each wall will deflect inward about 0.05 in., and prolonged operation at elevated temperatures will result in a slight permanent inward bow of the wall. Similar results were obtained in a supplemental calculation for a normal operating temperature of 900°F with a 200°F difference between the temperatures inner wall and the wall of the jacket. It will be important to heat the vessel uniformly and to avoid thermally shocking the vessel by excessive flow of cooling water in the compressed-air--water-spray coolant. Temperature excursions of ±135°F up to an extreme excursion of +360°F have been observed on an uncooled protion of the wall of the 5-in.-pipe reactor V102. V102 Mark II has more complete coverage of the walls by the cooling jacket, so the local wall temperature excursions should be minimized. The exit coolant temperature will be recorded for each channel to supplement the wall thermocouples in order to detect temperature excursions.

5. STUDIES ON THE CORROSIVITY OF NIOBIUM PENTAFLUORIDE

P. D. Miller*
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W. N. Stiegelmeyer*

5.1 Introduction

The work described in the following paragraphs was done to determine the corrosion resistance of several commercial alloys to NbF_5 under refluxing conditions. (The pure salt melts at 75.5°C and boils at 229°C.)

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*Battelle Memorial Institute

Since L-nickel was a preferred material of construction, it was used to make the vessel in which the study was carried out. Thus, the nickel container was a corrosion specimen. Then, additional coupon specimens of L-nickel, Monel, and INOR-8 were mounted in the vessel

5.2 Equipment and Procedure

The NbF_5 boiling vessel was made from an L-nickel tube, 1-1/2-in. in inner diameter and 18 in. long. The bottom was closed with a 1/4-in.-thick disk, using shielded arc welding and L-nickel filler wire. A 1/4-in. Monel Swage-Lok fitting was welded into the bottom plate so that a drain opening would be available at the conclusion of the experiment. The top closure, which was also welded, contained a 1/4-in. L-nickel thermocouple tube and a 1/4-in. Monel Swage-Lok fitting for filling operations.

The coupon specimens were fastened to the thermocouple tube before the top closure was welded to the vessel, and these specimens were placed so that pieces would be exposed at the vapor, interface, and liquid positions. The ones exposed in the vapor and liquid were approximately 1/2 x 3-1/2 in. Those exposed at the interface were about 1/2 x 7-1/2 in. These pieces contained a self-welded section at the lower area.

Figure 3 is a diagram of the apparatus used. It can be seen that the lower portion of the vessel was heated by a vertical electric furnace, while the top portion was thermostated by maintaining boiling water in a copper jacket brazed to the nickel tube. Also, appropriate fittings were provided, leading to a pressure gage, a source of fluorine, helium, and vacuum.

The NbF_5 (purchased from A. D. MacKay, Inc., 198 Broadway, New York 35, New York) had a minimum purity of 99%, and the impurities as determined by emission spectroscopy were:

Element	Impurities (ppm)	Element	Impurities (ppm)
Ta	500	V	100
Ti	300	Fe	50
Zr	300	Co	20
Si	100	B	1

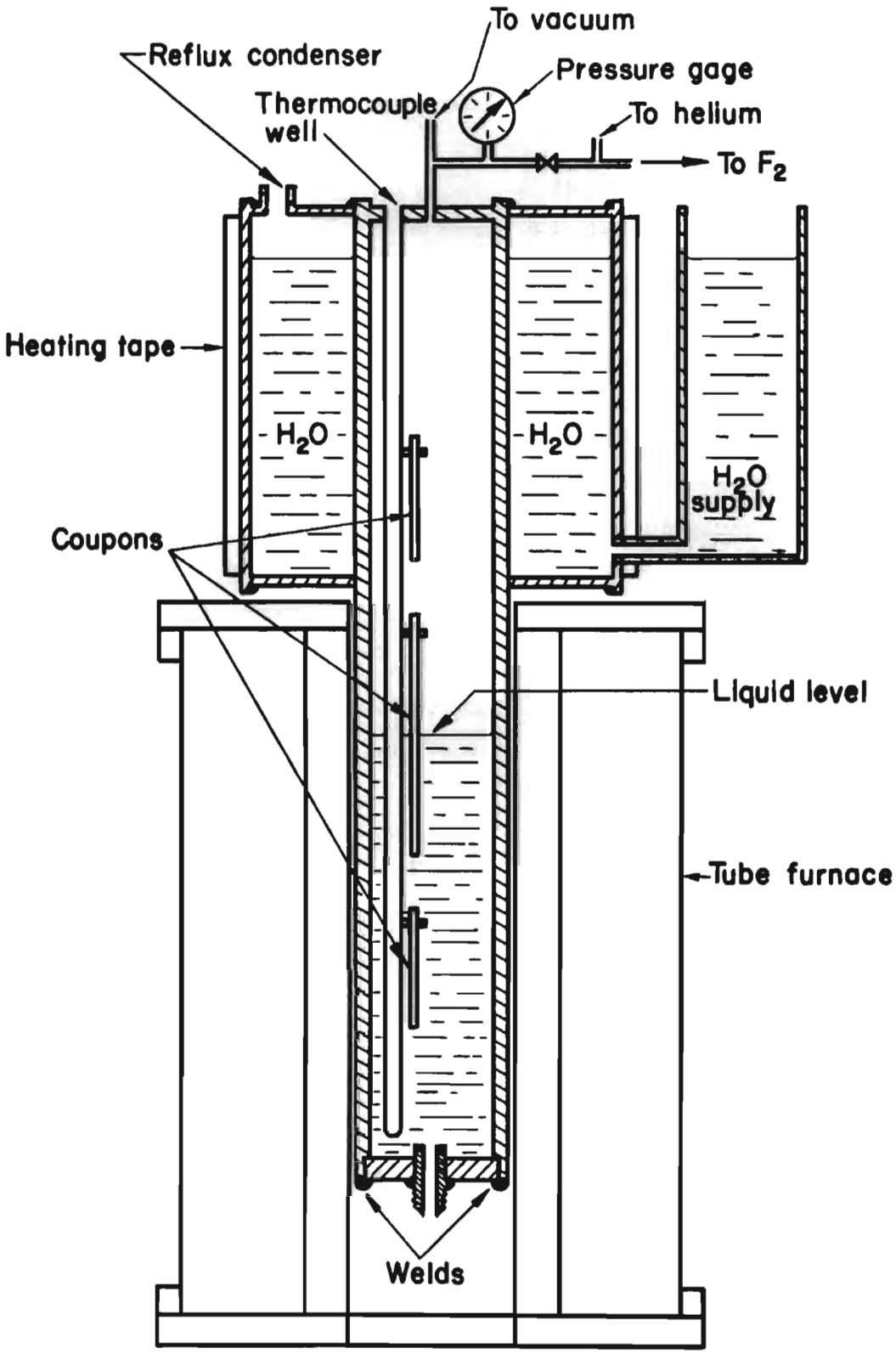


Fig. 3. Apparatus for Studying the Corrosivity of Refluxing NbF_5.

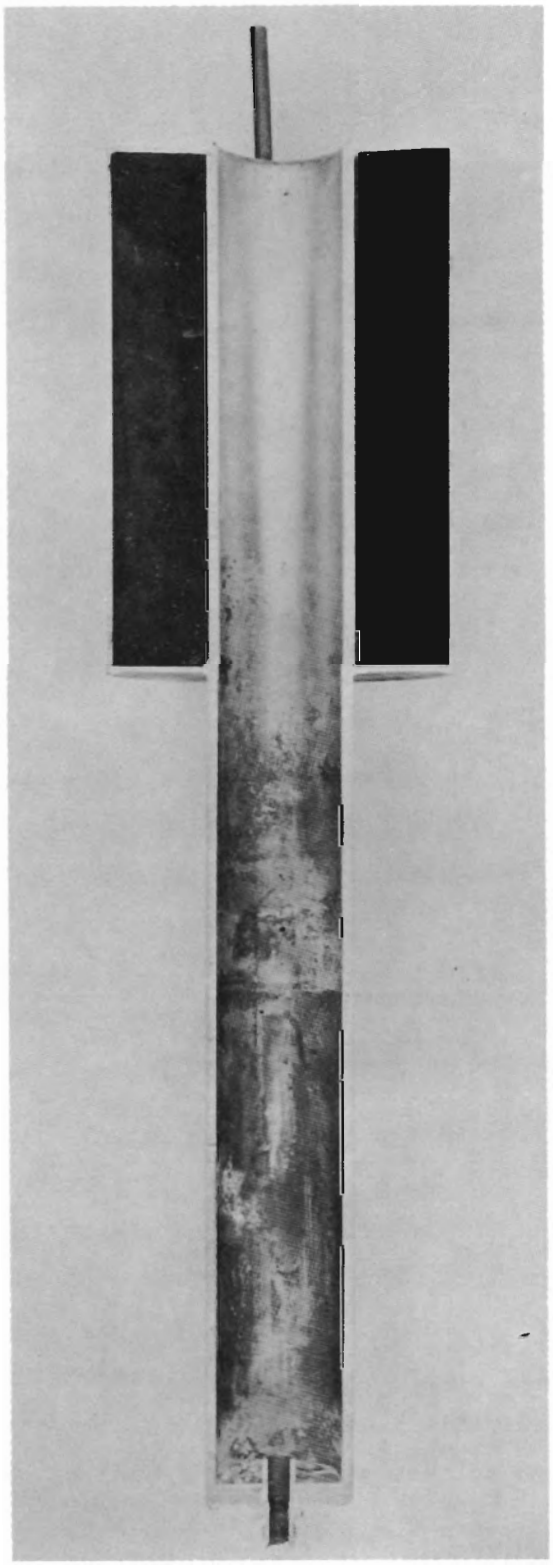
The loading of the NbF_5 was carried out in a dry box. The box and nickel boiling vessel were evacuated overnight, dry helium was then admitted, and the loading was carried out under this atmosphere. The salt was added as a dry powder through a funnel placed in the top opening in the nickel vessel. About 400 g of NbF_5 was added to the container.

At the beginning of the experiment, the vessel was evacuated and then filled with fluorine. The lower portion of the container was heated at 245°C initially to maintain boiling. It was necessary to increase the temperature gradually to 255°C during the 400 hr in order to maintain a constant temperature distribution above the boiling liquid. Condensation was provided by cooling the top with boiling water. Temperature readings on the thermocouple within the tube inside the container indicated a temperature of 105°C near the specimens in the vapor within the condenser. The pressure within the vessel rose gradually from 5 to 8.5 psig during the 405 hr of exposure.

At the conclusion of the experiment, a nickel vessel, 1-1/2 in. in inner diameter and 5 in. long, was attached to the bottom fitting on the boiler. The nickel receiver was evacuated, and, the boiler, under helium pressure, was heated to 105°C to melt the salt and allow it to flow into the receiver. The 361 g of NbF_5 recovered was shipped to ORNL.

5.3 Corrosion Results

The nickel boiling vessel was cleaned with water after the exposure. The top plate was removed by sawing, thus permitting withdrawal of the coupon specimens, and the vessel was then cut lengthwise into two pieces. Figure 4 shows one of these pieces. The top sections are clean and bright, with a slight etching. The liquid line, which was 6-1/2 in. from the bottom, is clearly visible. A second line attributed to vapor-liquid condensation was also visible about 1-1/2 in. above the liquid line. Some darkening of the surface of the lower portions of the tube can be seen. An examination of the area at the liquid-vapor interface, at low magnification, revealed that a small amount of roughening had taken place.



N97895

Fig. 4. Half-Section of NbF_5 Boiling Vessel and Condenser.

As to the coupons, they were cleaned in boiling 2.5% ammonium oxalate, rinsed, dried, and weighed. The most noticeable result on these pieces was a thin copper-colored deposit on the Monel specimens at areas exposed to the liquid. The deposit was not on the coupons of nickel and INOR-8, although a small amount was found on the wall of the nickel container vessel.

A very light etching of the metal was found on the coupons at the areas directly above the liquid-level line. The effect was least noticeable with Monel and greatest with nickel.

The corrosion rates, based on weight-loss measurements, are given in Table 2. It can be seen that in all cases the attack was more severe on the specimens exposed at the interface. However, the attack amounted to only about 0.6 mil/month for nickel, 0.4 mil/month for Monel, and 0.2 mil/month for INOR-8. The ranking was the same for the pieces exposed in the liquid. Very small variations in corrosion rates were measured for the pieces exposed in the vapor areas. Dimensionally, no detectable changes were found with a micrometer.

Table 2. Results of Corrosion by NbF_5

Alloy	Specimen Number	Exposure Location	Corrosion Rate, Based on Weight Loss (mil/month)
L-nickel:	NL-1	Vapor	0.09
	NL-2	Liquid	0.19
	NL-3	Interface	0.59
INOR-8:	NI-1	Vapor	0.08
	NI-2	Liquid	0.03
	NI-3	Interface	0.18
Monel:	NM-1	Vapor	0.10
	NM-2	Liquid	0.09
	NM-3	Interface	0.37

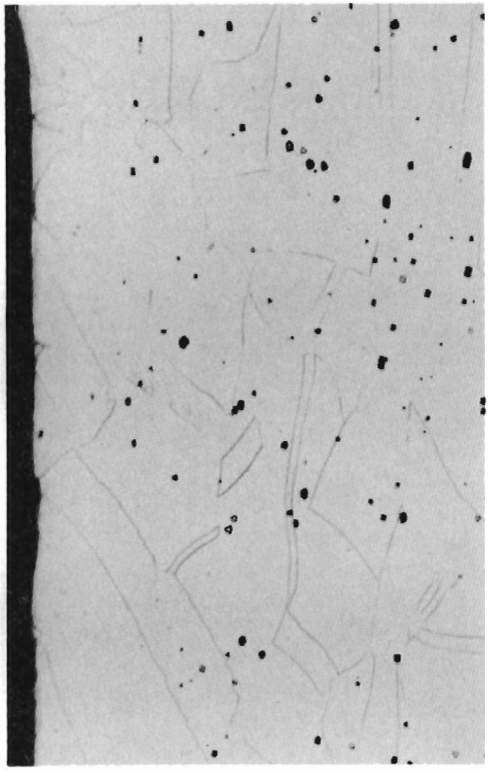
5.4 Metallographic Findings

Metallographic sections, taken from coupon specimens and from different parts of the vessel wall, were studied in the as-polished and etched condition.

The roughening that took place at the interface is readily seen at 250X. The distance from high to the low point on L-nickel was about 1 mil, which would correspond to a penetration rates of almost 2 mils/month. Figure 5 shows three sections of L-nickel. Figure 5a is a section taken from the vessel wall while in the as-received condition. Figure 3b is a longitudinal view of the vessel wall after exposure to NbF_5 at the interface position. The elongated shape of the grains is due to the rolling of the metal during tube fabrication. The absence of intergranular attack should be noted. Figure 5c illustrates a section of the 1/4-in. nickel tubing which formed the thermocouple well and specimen support. The roughening shown is quite similar to that found on the container wall. The surface of the nickel coupon was similar in appearance to that shown in Fig. 5c.

Specimens which had been exposed to the vapor and liquid only were not roughened.

No preferential attack occurred at the welds on any of the coupons. The most deleterious effect noted with nickel occurred on the bottom plate and container wall. Intergranular attack was found in these areas and is illustrated in Fig. 6. Etching was required to bring out the apparent penetration, which extends to a maximum depth of 2-1/2 mils (about 4.5 mils/month). A very slight amount of intergranular attack was also found near the welds on the bottom of the 1/4-in. thermocouple tube. As was mentioned before, no intergranular attack was found on the welded coupons which were suspended farther up in the salt. Thus, it appears that the intergranular effects were confined to the bottom sections of the vessel. Since no intergranular attack was found on the external surfaces, it appears that the penetration did not take place during welding.

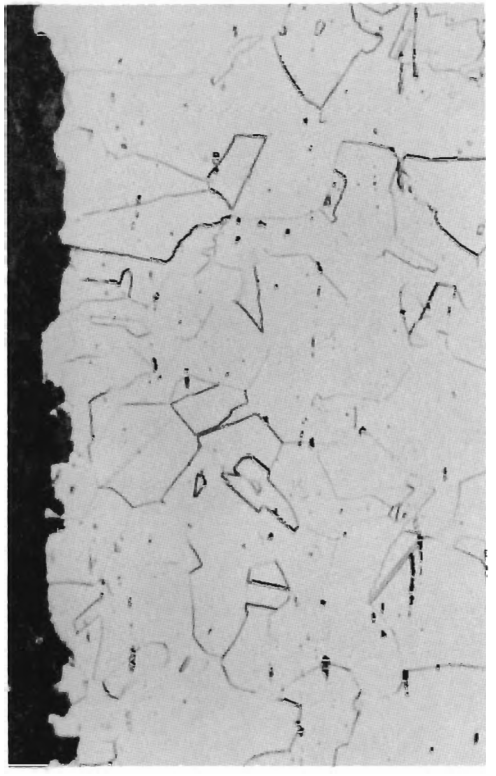


250X C1952

a. Specimen of As-Received Nickel Container

250X C1953

b. Longitudinal View of Interface Area of Nickel Container After Exposure to NbF_5

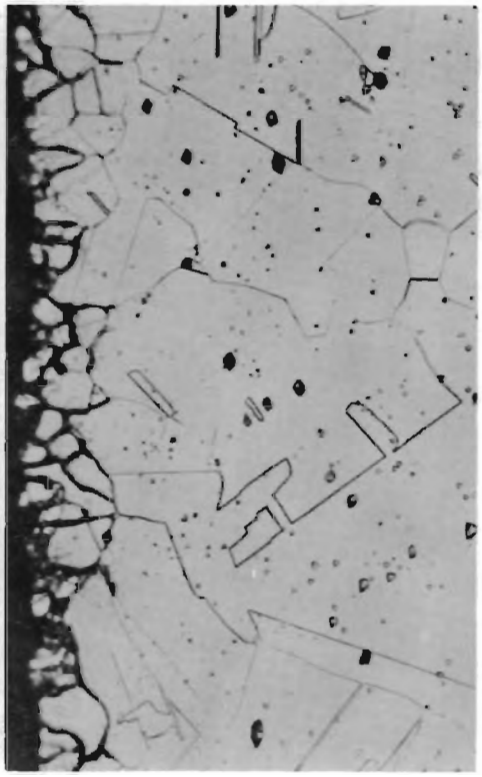


250X C1954

c. Outer Surface of Nickel Sparge Tube After Exposure at Interface in NbF_5

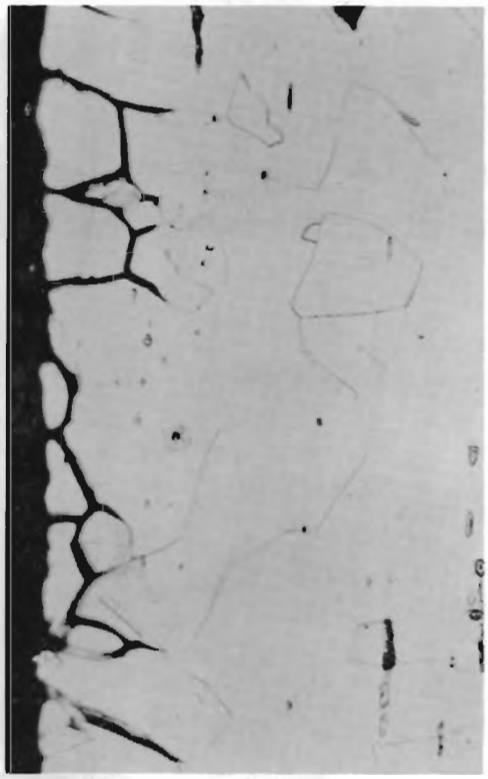
Etchant: equal parts of glacial acetic acid and nitric acid. The roughening which took place at the interface was about 1 mil deep at maximum points.

Fig. 5. Sections from Nickel Specimens.



250X C1955

a. Section From Bottom Plate



250X C1956

b. Section From Container Wall

Etchant: equal parts of glacial acetic acid and nitric acid. The intergranular penetration extends to a depth of about 2-1/2 mils.

Fig. 6. Section from Lower Portion of Nickel Container.

It has been concluded that the attack is a result of aggressive impurities concentrated at the bottom of the bath, combined with a susceptibility produced during welding.

The thin deposit of copper, which was found on the submerged portion of the Monel specimens, is shown in cross section in Fig. 7a. This layer is very thin, about 0.1 mil. No obvious damage occurred to the microstructure of the Monel as a result of the transfer of copper. Figure 7b illustrates the appearance of the section when etched to reveal the grain boundaries. The small pit, visible in the top portion of the photograph, is about 0.5 mil deep, which corresponds to a penetration rate of about 1 mil/month.

A few small areas of intergranular penetration, up to 1 mil deep, were found in the Monel fitting which was welded into the bottom plate.

As can be seen in Fig. 8, the INOR-8 specimens were very resistant to the environment and showed no intergranular effects and very little roughening.

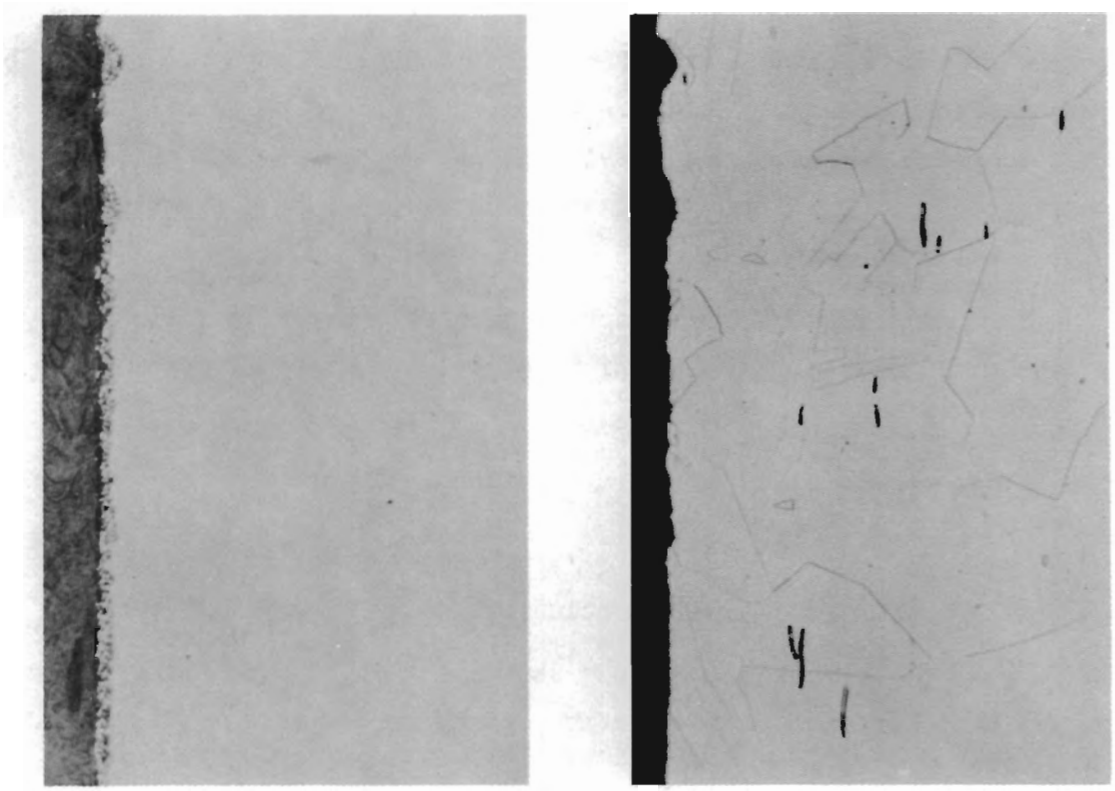
5.5 Conclusions

The present corrosion study has shown that any of the three candidate materials would be satisfactory in the system contemplated. The rankings are listed below.

1. The optimum material, based on both weight-change measurements and metallography, is INOR-8.

2. The fact that copper is plated out on Monel indicates incomplete immunity, although such deposits are frequently found to enhance corrosion resistance. The effect was not noticeably harmful in the present experiment, and would become serious only if the layer grew progressively to the point where pieces flaked off and where base metal, itself, were severely leached.

3. Nickel is rated lowest. The surface roughening at the interface is most severe for this metal, and its susceptibility to intergranular attack is also a detrimental factor.

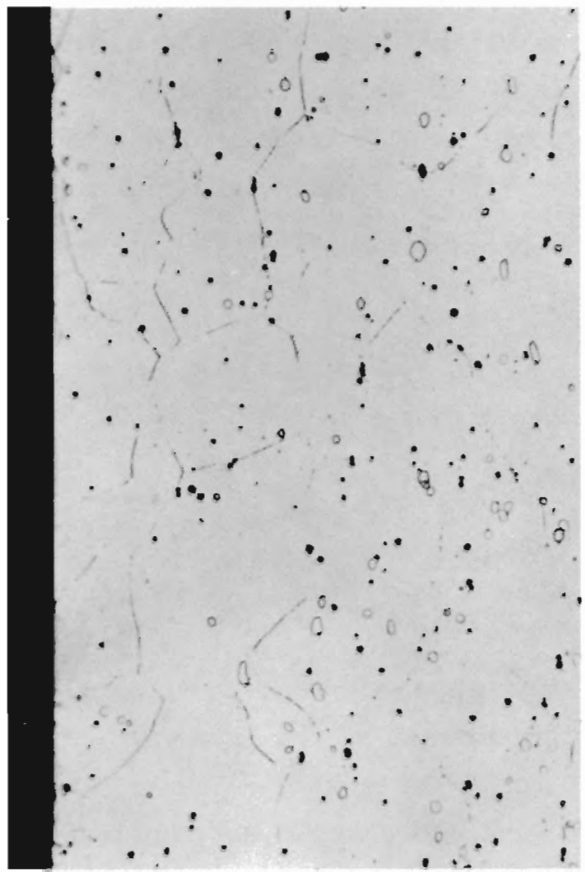


250X C1957 250X C1958

a. Unetched Section b. Etched Section

Etchant: equal parts of glacial acetic acid and nitric acid. Note the thin layer of copper deposit on the unetched section.

Fig. 7. Structure of Monel Specimen After Exposure at Interface.



250X C-1959

Etchant: 7 parts chronic acid, 3 parts HCl.

Fig. 8. Structure of INOR-8 Specimen After Exposure at Interface.

6. AQUEOUS PROCESSES FOR RECOVERING URANIUM FROM ROVER FUEL COMBUSTION ASH

L. M. Ferris K. S. Warren

6.1 Combustion of Irradiated Rover Fuel

Equipment for studying the fate of fission products during the burning of Rover fuel in oxygen has been assembled and partially cold-tested. The results of the cold tests indicate that the equipment will be suitable for use in the forthcoming hot-cell experiments with Kiwi-B4A fuel specimens. The hot-cell tests are tentatively scheduled to begin on May 15, 1963.

7. CHLORINATION AND CHLORIDE VOLATILITY STUDIES ON THE RECOVERY OF URANIUM FROM ROVER FUEL COMBUSTION ASH

J. R. Flanary J. H. Goode

7.1 Flowsheet Demonstration on Radioactive Fuels: Chloride Volatility Process

Exploratory experiments were made in a "warm" call on the adaptation of chloride volatility systems to the recovery and decontamination of uranium contained in spent Rover fuel elements. By using operating conditions expected to give optimum recovery, conditions that had been determined on unirradiated UO_2 and sectioned Rover rods, two hot runs were made with 1-in.-long sections of irradiated Kiwi-B4A elements, decayed for about five months. These preliminary experiments showed reasonable separation of niobium from the uranium, but with gross-gamma decontamination factors of only about 2. Ruthenium and zirconium-niobium appeared to be the principal contaminants in the uranium product, while 1 to 2% of the uranium was found in the separated niobium and volatile fission product fraction.

Using a 2-in.-diam tube furnace and a Vycor tube divided into about four 6-in.-long sections by quartz cloth filters, the following procedure was followed:

1. A section of fuel rod was burned in pure oxygen, at a tube temperature of 600°C, for 2.5 hr to convert uranium, niobium, and fission products to oxides and to eliminate the graphite.

2. The oxides were chlorinated with Cl_2--15% CCl_4 vapor, at 500°C, for about 2.5 hr to convert to a volatile chloride form that moved through the filter into the next cool section of tube outside the furnace, leaving the nonvolatile fission product chlorides behind.

3. After moving the section containing the uranium, niobium, and volatile fission products into the furnace, which had been cooled to 300°C, the solids were rechlorinated with Cl_2--15% CCl_4 to effect a separation from the fission products not volatile at the lower temperature.

4. After cooling the furnace to room temperature, a slow stream of inert gas (argon) was passed through the tube to purge the Cl_2-CCl_4 vapors, and the temperature was then increased to 400°C over a 30- to 40-min period. The nonvolatile uranium remained behind, and the volatile niobium chloride and fission products moved through a series of filters into a cool section outside the furnace.

5. A diamond wheel was then used to cut the Vycor tube into sections A, B, C, and D, corresponding to the fractionation steps described above. Each section was then leached with suitable reagents to dissolve the contents, and the solutions were sampled. Samples from 4 M NaOH scrubber solutions were also taken during the tests.

7.2 Recommendations Leading to the Development of a Flowsheet

Chemical and radiochemical analyses indicated that additional laboratory data from unirradiated and tracer-level experiments are needed before a chloride volatility flowsheet can be set down. Results of the runs showed that:

1. The tracer quantities of plutonium partially followed the uranium through the two chlorinations, with a partial separation during the second chlorination at 300°C;

2. Burning in oxygen, flowing in a direction opposite to that of the Cl_2-CCl_4 vapors, gave a partial separation of a pure ruthenium oxide. The RuO_4 was collected just outside the furnace on a glass-wool plug in the Vycor tube;

3. The rare earths and some ruthenium appeared to make up the major fraction of nonvolatile fission products found in tube sections A and B.

4. A change in procedure is needed to keep all the uranium product in section C in order to reduce the 1 to 2 % loss to the volatile components found in section D. At the same time, a means of increasing the volatility of the fission products contaminating the uranium product in section C (i.e., ruthenium and zirconium-niobium) must be developed.

Two additional runs are to be made under the same conditions but with more highly irradiated UO_2 as feed material. These runs will serve to point out the various routes of the fission products during the chloride volatility steps.