CLADDING HULL DECONTAMINATION PROCESS --
PRELIMINARY DEVELOPMENT STUDIES

B. Griggs
G. H. Bryan

December 1979

Prepared for
the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Richland, Washington 99352

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ABSTRACT

An investigation of the chemical and radioactive properties of fuel hulls was conducted to assist in a decontamination process development effort. The removal of zirconium oxide layers from zirconium was accomplished by a treatment in 600°C HF followed by a dilute aqueous reagent. Similar treatment in fused alkali-zirconium fluoride salt baths was examined. A remotely operated small batch facility was developed and process parameters determined.

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INTRODUCTION

The traditional method for processing irradiated power reactor fuel elements to recover the contained fuel value involves chopping the zirconium alloy clad elements into one- to three-inch lengths and leaching them in hot nitric acid to dissolve the contained uranium dioxide. The residue from this operation includes the metallic fuel clad pieces, springs, insoluble insulation pellets, and miscellaneous fuel element hardware that are unaffected by the hot nitric acid. These residues, called hulls, are contaminated by 0.01 to 0.5 wt% of original fuel remaining attached to surfaces, smeared in cuts, etc., which clearly classes this material as transuranic waste contaminated by more than 10 nCi/g (USERDA 1976). The makeup of the hull stream will vary depending on the reactor type, degree of disassembly before shearing, and age (newer fuels tend to contain more zirconium alloys). Approximately 22% of the weight of a fuel bundle is metal with about 288 Kg Zr/MTHM, 29 Kg stainless steel/MTHM, and 8 Kg Inconel/MTHM. The effective density of the leached Zircaloy tube sections is somewhat less than 1 g/ml, resulting in a volume of about 0.3 m³/MTHM.

These hulls represent a low density, leachable, chemically reactive, transuranic waste. Placing this material in a suitable condition for storage requires either adding encapsulating material such as concrete or lead, which increases the mass of the transuranic waste form, or densification and surface area reduction by melting, which decreases the waste stream volume, leachability, and chemical reactivity. Most of the current concern with this potential waste involves its transuranic element contamination and its chemical reactivity.

A review of potential methods for clad hull treatment has been published (USERDA 1976). The methods reviewed were:

- encapsulation and storage or disposal
- compaction and encapsulation
- matrix formation (with or without compaction) and encapsulation
- melting (with and without cleaning)
- chemical reaction to chloride, fluoride, oxide, or sulfate and encapsulation
- conversion into an absorbent for high level waste and encapsulation.

The various methods were discussed but no attempt was made to select the best method. Each method has characteristics that make it desirable for certain aspects of waste treatment and disposal. The decontamination and melting treatment characteristics make it the only process capable of producing a usable (though radioactive) metal product, which is also the most dense form of the secondary hull waste products. This melting process densifies the metallic waste to 6.5 g/ml from less than 1 g/ml thus producing a reduction in volume of 6.5, which is reduced to the extent other secondary wastes are produced. Melt densification also reduces the surface area per unit mass available for leaching by a factor of 75, increases thermal conductivity several orders of magnitude, and decreases radiation shielding requirements for transport in terms of mass shielding per unit mass of hulls.

The ductility, hardness, and corrosion resistance of zirconium alloys are substantially affected by alloying with oxygen, nitrogen, or many other impurities. If hulls are melted as retrieved from the dissolver, they will alloy with the substantial surface oxides of zirconium, iron, nickel, uranium, fission products, activation products, etc. The removal of surface oxides and contamination before melting could result in a metallurgically sound material which, even though mildly radioactive after a few years, could be used in a controlled environment in the nuclear industry. If the melting process could

remove the small quantity of transuranic elements uniformly distributed in the metal, the surface cleaning and melting process could result in a non-transuranic metal plus a small amount of transuranic waste.

A review of the state-of-the-art and possible treatment (Griggs 1974) sequences to decontaminate the hull waste was conducted and it was found that it might be possible to clean and melt this waste into a metal ingot with a minor transuranic waste by-product. When the program began, there were no known chemical methods of removing zirconium oxide from zirconium alloys and commercial melting practice was not easily adapted to melting radioactive materials. Even the characteristics of a "hull" were poorly defined. A laboratory program was initiated to develop and test processes for cleaning, melting, and casting the hull waste stream into usable forms. The results of these efforts have been routinely reported in quarterly reports (PNL Quarterly Report List) and several topical reports (Nelson, Schlienger, and Tiesenhansen 1976; Zima 1976; Nelson and Griggs 1976; Dillon, Griggs, Kemper, and Nelson 1976; Zima 1977; Dillon 1977). Recently Jenkins and Taylor (1977) examined hull characteristics and simple surface chemical decontamination techniques which remove part of the residual fuel but do not produce a non-transuranic waste. This report covers the initial development of the chemical decontamination process.

PROCESS DEFINITION

The design of a decontamination process for fuel hulls requires an accurate description of the waste stream. An attempt to describe the waste stream (Griggs 1974) involved a considerable amount of deduction and speculation because data were not available. In order to more closely estimate the properties of cladding hulls, irradiated fuel cladding was treated in boiling 8 M HNO_3 to simulate head end treatment and rinsed in 8 M HNO_3 and H_2O . The resulting "hulls" should resemble the planned waste stream hulls with the exceptions that (1) they were carefully and individually handled and (2) the "dissolver solution" was much lower in dissolved fuel concentration and higher in HNO_3 concentration than a normal dissolver solution. The PWR-1 hull, which was treated along with a batch of its fuel, is an exception. It was necessary to simulate fuel hulls because there were no operating fuel reprocessing plants where actual fuel hulls could be obtained. The only previously generated fuel hulls in the U.S. were stored at the Nuclear Fuel Service plant and were not available.

Three distinct types of fuel cladding were obtained from hot cell waste. One type exposed to about 24,000 MWD/MTHM in an early BWR was obtained from General Electric Co. A second type, exposed in a PWR to about twice this exposure ($\sim 58,000$ MWD/MTHM), was obtained from Westinghouse Electric Co. A third type was obtained from a mixed oxide fuel rod exposed about 24,000 MWD/MTHM in Saxton reactor. The BWR and Saxton cladding were aged five to six years since discharge while the PWR cladding was less than two years since discharge.

CHEMICAL CHARACTERISTICS

The chemical characteristics of the cladding are fairly well known from the many fuel examinations that have been made and from Zircaloy technology in general. The Zircaloy clad is coated both inside and outside with a layer of zirconium oxide, which is relatively inert to most aqueous solutions. The inside oxide layer is derived from fuel outgassing during operation and is relatively thin, about 1 to 10 microns (Megerth 1971). The oxide layer on the outside of the Zircaloy will run between 10 and 100 microns and is formed by

reaction with the reactor coolant. Shearing of the Zircaloy-clad fuel rods will tend to fracture the protective oxide layers near the shear cut as well as expose a fresh metal surface in the cross section. Zircaloy and zirconium oxide are relatively inert to the dissolver solution and will emerge from the dissolver unchanged. Certain alloys of zirconium with beryllium (Schulz 1972), uranium (Roth 1952), and presumably other metals will undergo a selective corrosion in the dissolver solution which dissolves one phase of the alloy and leaves a finely divided zirconium that is pyrophoric. A review of zirconium alloy hull pyrophoricity has been completed by Levitz (1975) and Kullen (1977).

The Zircaloy is generally alloy 2 in BWRs and alloy 4 in PWRs. The stainless steel is usually Type 304. The Inconels are Type X, 718, and 600. Future fuel designs may replace some of the stainless steel and Inconel with Zircaloy.

RADIOACTIVE CHARACTERIZATION

The simulated fuel hulls were characterized by determining the amount of transuranic contamination that could be readily leached from the surface by a practical reagent, the amount incorporated in the oxide layer, the amount diffused into the metal, and the amount uniformly distributed in the base metal. Answers to these questions allow one to determine the necessary decontamination steps to remove the transuranic contamination. These analyses were conducted by leaching in a decontamination solution then dissolving residual oxide and metal in another solution. Mechanical removal of the oxide layer on a similar piece followed by a light chemical etch and dissolution of the decontaminated base metal in two or more steps was undertaken to establish base metal TRU content and whether significant diffusion of TRU from the surface took place. The base metal values thus determined could be subtracted from the previous sample analyses to determine the amount contained in the oxide layer and the adjacent metal (~1 mil). Detailed analyses of the solutions generated for transuranics and identifiable gamma emitters were made.

The hulls were leached in a decontamination solution (Meservey 1970) for several two-hour periods to determine how much activity was easily removable

with a decontamination solution. These solutions were analyzed for total alpha activity and a composite solution was analyzed for transuranic elements and significant fission products. Figure 1 shows the removal of surface alpha activity versus time for this treatment of the hulls. More complete analytical data are in Table 1 for a composite of the surface leaching samples. These analyses show that the leaching removes about one-half of all the activity on the specimen except the activated base metal isotopes, such as ^{124}Sb , ^{95}Zr , and ^{95}Nb .

In general, the leached radionuclides are the same as the ones incorporated in the surface oxide layer and reflect the fuel contamination source. Most of the residual radionuclides from the leaching step are contained in the surface oxide layer as shown in Table 1. The amount contained in surface layers was determined by dissolving one leached hull and an adjacent piece of base metal. The subtraction of the base metal value from the total leached piece results in the amount contained in surface layers.

FIGURE 1. Leaching of Surface Activity From Fuel Holes

TABLE 1. Analyses of Simulated Fuel Hulls

	ANALYSIS ①		SURFACE LEACH ②			SURFACE OXIDE PLUS THIN METAL LAYER ③			BASE METAL ④			ACTIVITY RATIO TOTAL TO BASE METAL		
	TYPE	UNITS ⑤	PWR-1 ⑥	PWR-2 ⑦	BWR ⑧	PWR-1	PWR-2	BWR	PWR-1	PWR-2	BWR	PWR-1	PWR-2	BWR
a	TOTAL	nCi/cm ²	9.5×10 ³	9.9×10 ²	1.2×10 ¹	6.4×10 ³	9.9×10 ²	3.0×10 ⁰	1.2×10 ¹	3.1×10 ⁰	3.7×10 ⁰	1.3×10 ³	6.4×10 ²	5.0×10 ⁰
		nCi/g	2.3×10 ⁴	2.3×10 ³	2.0×10 ¹	1.6×10 ⁴	2.3×10 ³	5.0×10 ⁰	2.9×10 ¹	7.2×10 ⁰	6.2×10 ⁰	1.3×10 ³	6.4×10 ²	5.0×10 ⁰
U	TOTAL	ng/cm ²	1.2×10 ⁵	3.8×10 ⁴	9.8×10 ²	8.4×10 ⁴	3.5×10 ⁴	4.3×10 ³	1.1×10 ²	7.0×10 ²	4.0×10 ²	1.9×10 ³	1.1×10 ²	1.4×10 ¹
	TOTAL	nCi/g	6.1×10 ⁻¹	6.6×10 ⁻²	4.5×10 ⁻³	3.2×10 ⁻¹	6.4×10 ⁻²	1.4×10 ⁻²	6.0×10 ⁻³	1.6×10 ⁻³	5.0×10 ⁻²	1.6×10 ²	8.2×10 ¹	1.4×10 ⁰
	233	at %	1.5×10 ⁻⁴	---	6.0×10 ⁻³	4.0×10 ⁻⁴	---	---	1.9×10 ⁻¹	1.2×10 ⁻¹	5.9×10 ⁻¹	---	---	---
	234	at %	1.8×10 ⁻²	6.0×10 ⁻³	2.4×10 ⁻²	1.9×10 ⁻²	6.7×10 ⁻³	2.2×10 ⁻²	3.8×10 ⁻²	9.9×10 ⁻³	4.8×10 ⁻²	---	---	---
	235	at %	9.4×10 ⁻¹	5.5×10 ⁻¹	2.2×10 ⁰	9.6×10 ⁻¹	5.9×10 ⁻²	2.1×10 ⁻³	1.4×10 ⁻¹	5.6×10 ⁻¹	3.7×10 ⁻¹	---	---	---
	236	at %	9.7×10 ⁻¹	4.7×10 ⁻²	4.2×10 ⁻¹	9.6×10 ⁻¹	4.8×10 ⁻²	4.3×10 ⁻¹	1.1×10 ⁻¹	4.1×10 ⁻²	7.0×10 ⁻²	---	---	---
	238	at %	9.8×10 ¹	9.9×10 ¹	9.7×10 ¹	9.8×10 ¹	9.9×10 ¹	9.9×10 ¹	9.9×10 ¹	9.9×10 ¹	9.9×10 ¹	---	---	---
Pu	TOTAL	ng/cm ²	4.5×10 ³	4.5×10 ³	3.0×10 ¹	3.3×10 ³	6.2×10 ³	3.1×10 ²	6.4×10 ⁰	2.4×10 ¹	1.2×10 ¹	1.2×10 ³	4.5×10 ²	2.9×10 ¹
	TOTAL	nCi/g	4.4×10 ³	1.3×10 ³	9.9×10 ⁰	3.0×10 ³	1.8×10 ³	7.0×10 ¹	3.9×10 ⁰	4.9×10 ⁰	2.7×10 ⁰	1.9×10 ³	6.5×10 ²	3.1×10 ¹
	238	at %	1.8×10 ⁰	2.5×10 ⁻¹	5.5×10 ⁻¹	1.8×10 ⁰	2.5×10 ⁻¹	8.4×10 ⁻¹	1.0×10 ⁰	7.0×10 ⁻²	3.6×10 ⁻¹	---	---	---
	239	at %	4.9×10 ¹	7.3×10 ¹	6.8×10 ¹	4.9×10 ¹	6.9×10 ¹	6.4×10 ¹	5.2×10 ¹	8.5×10 ¹	6.9×10 ¹	---	---	---
	240	at %	2.2×10 ¹	1.8×10 ¹	1.9×10 ¹	2.2×10 ¹	1.8×10 ¹	2.0×10 ¹	2.0×10 ¹	1.1×10 ¹	2.0×10 ¹	---	---	---
	241	at %	1.6×10 ¹	9.6×10 ⁰	8.8×10 ⁰	1.6×10 ¹	1.0×10 ¹	1.0×10 ¹	1.7×10 ¹	3.7×10 ⁰	8.3×10 ⁰	---	---	---
	241	nCi/g	1.7×10 ⁵	1.0×10 ⁵	4.3×10 ²	1.2×10 ⁵	1.4×10 ⁵	3.0×10 ³	2.5×10 ²	2.0×10 ²	1.5×10 ²	1.1×10 ³	1.1×10 ³	2.4×10 ¹
	242	at %	1.1×10 ¹	1.6×10 ⁰	3.2×10 ⁰	1.1×10 ¹	1.7×10 ⁰	4.5×10 ⁰	1.1×10 ¹	3.3×10 ⁻¹	2.6×10 ⁰	---	---	---
Am	241	nCi/cm ²	3.1×10 ²	---	4.5×10 ⁰	2.1×10 ²	---	1.6×10 ⁰	3.8×10 ⁻¹	1.3×10 ⁰	1.7×10 ⁰	1.4×10 ³	---	4.6×10 ⁰
	241	nCi/g	7.4×10 ²	---	7.5×10 ⁰	5.0×10 ²	---	2.6×10 ⁰	9.0×10 ⁻¹	3.0×10 ⁰	2.8×10 ⁰	1.4×10 ³	---	4.6×10 ⁰
	243	nCi/cm ²	3.0×10 ¹	---	2.6×10 ⁻²	1.6×10 ¹	---	2.0×10 ⁻¹	2.7×10 ⁻²	---	6.0×10 ⁻³	1.7×10 ³	---	3.8×10 ¹
	243	nCi/g	7.2×10 ¹	---	4.4×10 ⁻²	3.8×10 ¹	---	3.4×10 ⁻¹	6.4×10 ⁻²	---	9.9×10 ⁻³	1.7×10 ³	---	3.8×10 ¹
Cm	242	nCi/cm ²	2.8×10 ³	---	5.4×10 ⁻²	2.0×10 ³	---	3.8×10 ⁻¹	3.2×10 ⁰	8.2×10 ⁻³	1.7×10 ⁻²	1.5×10 ³	---	2.7×10 ¹
	242	nCi/g	6.8×10 ³	---	9.0×10 ⁻²	4.9×10 ³	---	6.4×10 ⁻¹	7.7×10 ⁰	1.9×10 ⁻²	2.9×10 ⁻²	1.6×10 ³	---	2.7×10 ¹
	244	nCi/cm ²	3.1×10 ³	---	1.5×10 ⁰	2.0×10 ³	---	7.6×10 ¹	7.3×10 ⁰	1.4×10 ⁻²	3.3×10 ⁻¹	7.0×10 ²	---	5.4×10 ¹
	244	nCi/g	7.4×10 ³	---	2.6×10 ⁰	4.9×10 ³	---	2.7×10 ¹	1.7×10 ¹	7.9×10 ⁻²	5.5×10 ⁻¹	7.0×10 ²	---	5.4×10 ¹
Th	228	nCi/cm ²	---	---	---	---	---	---	---	---	7.0×10 ⁻²	---	---	---
	232	ng/cm ²	---	---	---	---	---	---	---	---	1.7×10 ²	---	---	---
	232	ng/g	---	---	---	---	---	---	---	---	2.9×10 ²	---	---	---
Mn	54	nCi/cm ²	---	---	---	4.9×10 ³	2.0×10 ²	---	2.0×10 ⁴	3.5×10 ²	1.2×10 ²	1.2×10 ⁰	1.6×10 ⁰	---
Co	60	nCi/cm ²	---	---	1.9×10 ²	2.3×10 ⁴	4.5×10 ²	---	2.0×10 ⁴	2.8×10 ³	8.0×10 ³	2.1×10 ⁰	1.2×10 ⁰	---
Zr	95	nCi/cm ²	---	---	---	1.2×10 ⁴	---	---	8.2×10 ⁴	---	---	1.1×10 ⁰	---	---
Nb	95	nCi/cm ²	---	---	---	2.1×10 ⁴	---	---	1.8×10 ⁵	---	---	1.1×10 ⁰	---	---
Ru	106	nCi/cm ²	3.2×10 ⁵	---	1.6×10 ³	7.2×10 ⁵	---	1.4×10 ³	---	---	---	---	---	---
Sn	113	nCi/cm ²	---	---	---	5.1×10 ³	---	---	3.7×10 ⁴	---	---	1.1×10 ⁰	---	---
Sb	125	nCi/cm ²	---	5.1×10 ³	2.4×10 ³	7.5×10 ⁴	---	---	7.8×10 ⁵	1.3×10 ⁵	7.6×10 ⁴	1.1×10 ⁰	1.0×10 ⁰	1.1×10 ⁰
Cs	134	nCi/cm ²	1.8×10 ⁶	3.1×10 ⁵	2.4×10 ³	5.4×10 ⁵	8.9×10 ⁴	2.1×10 ³	5.2×10 ¹	4.4×10 ⁰	---	4.5×10 ⁴	9.1×10 ⁴	---
	137	nCi/cm ²	1.8×10 ⁶	9.4×10 ⁵	2.9×10 ⁴	6.1×10 ⁵	9.2×10 ⁵	2.9×10 ⁴	6.7×10 ¹	6.2×10 ²	3.0×10 ²	3.6×10 ⁴	3.0×10 ³	1.9×10 ²
Ce	144	nCi/cm ²	8.7×10 ⁴	---	4.6×10 ²	2.7×10 ⁵	---	7.6×10 ²	---	---	---	---	---	---
Eu	154	nCi/cm ²	---	---	6.5×10 ²	1.6×10 ⁴	---	6.5×10 ²	---	---	---	---	---	---

NOTES TO TABLE 1

- Analyses were performed by separation of some spiked fractions, alpha energy analyses, mass spectrometry, and gamma energy analyses as appropriate by the Analytical and Nuclear Research Section of PNL.
- The hull produced by leaching in boiling 8 M nitric acid was leached further in a solution of:

0.4 M Ammonium Oxalate
 0.16 M Ammonium Citrate
 0.1 M Ammonium Fluoride
 0.3 M Hydrogen Peroxide

With the pH adjusted to 5 and heated to 90-95°C for 12 hours (PWR-1 and BWR) and 4 hours (PWR-2). Analyses of this leaching solution is reported here.

- The hull, leached as described in Note 2, was dissolved in nitric (32%) hydrofluoric acid (3%) solution. Small additions of 48% HF were made to the residue to bring the complete sample into solution. Adjacent base metal analysis was subtracted.
- A hull sample adjacent to the one used in Notes 2 and 3 was mechanically abraded to remove surface oxide. The piece was subsequently given several short (<30 sec.) etches in room temperature 33% HNO₃-2% HF solution followed by a 70% HNO₃ dip and water rinse. Total metal removal was estimated at 0.003 cm (10⁻³ in.). The residual specimen was dissolved in 32% HNO₃-3% HF solutions in two steps, and solution was analyzed separately. The results of the analyses are averaged and/or selected in these columns and in general agree very closely.
- The units of comparison selected here are nanocuries or nanograms per square centimeter of internal surface area of the original hull or nCi/g of original hull weight even though the portion analyzed was an inner section of the hull. The following weight and area ratios were used.

	PWR-1	PWR-2	BWR
g/cm ² Internal Area	0.41	0.43	0.60
g/cm ² Total Area	0.19	0.19	0.27
Internal Area/Total Area	0.46	0.44	0.40

- Obtained from a commercial reactor fuel nominally exposed 55 MWD/kg in 4.8 years with an original enrichment of 5.8 w/o ²³⁵U. Discharged October 1973--analyses corrected to June 1975.
- Obtained from a 6.6 w/o mixed oxide fuel rod exposed about 19.7 MWD/kg in 2.8 years at Saxton reactor. Discharged October 1968 with analyses corrected to November 1974.
- Obtained from a fuel rod exposed about 24.1 MWD/kg in Big Rock Point reactor. Discharged data unknown with analyses corrected to April 1978. Calculations indicate most of the exposure was before 1969.

The base metal values were determined by mechanically removing the surface oxide from the hulls and chemically removing a small amount of metal, usually about 0.003 cm (1 mil). Base metal activity from activated impurities is so low compared to the surface activity that thorough decontamination was necessary. The residual piece was dissolved in two steps to check for contamination or diffusion. No evidence of actinide or fission product diffusion deeper than the 0.003 cm (1 mil) removed metal was found. Careful checks and controls were applied to avoid and monitor the contamination of solvents with uranium and thorium.

The radioactive description of a "hull" can be developed from a review of Table 1. It shows that the simulated fuel hulls contain less than 0.01% of the original fuel based on the surface uranium content. Cesium content is from 3 to 90 times higher than one would predict from the fuel content of the leached hull. In PWR hulls, about 99.9% of the actinides are contained in or on the surface oxide layers. The well-aged, leached (HNO_3) BWR hull contained only about 80% of the actinides in the surface layers. This is because the metal contained more uranium impurity and the surface oxides were more easily leached in nitric acid. This relationship is shown graphically in Figure 2. We do not consider these differences to be caused by the type of reactor exposure (in PWR or BWR).

FIGURE 2. α Activity Distribution in Fuel Hulls Determined by Solution Analyses. *The α activity in the outer corrosion product layer was not determined separately from the inner corrosion product layer and was assumed to be low. Jenkins (Jenkins and Taylor, 1977) found less than 8% on the outside surface.

Zircaloy contains small amounts of uranium and thorium impurities. Irradiation of these impurities give rise to transuranic elements uniformly distributed in the Zircaloy. Calculation of the expected quantities by the ORIGEN (Bell 1973) computer code was conducted (Griggs 1974) for a hypothetical fuel clad with Zircaloy containing 1 ppm uranium impurity and a standard (33 MWD/Kg) exposure. Results of this calculation indicated more than 10 nCi/g of transuranic elements would be generated from this impurity, mostly the beta emitter ^{241}Pu . Very careful analyses of the base metal from the hulls were conducted to determine the level of transuranic elements generated from impurity uranium and thorium during irradiation. The existence of these elements in the predicted concentrations was established as shown in Table 1. A further check was made by running the ORIGEN program with appropriate data on the impurity level, irradiation, and storage history to compare predicted and observed transuranic element concentrations. Table 2 shows a pertinent selection of these runs for PWR-1 and PWR-2 hulls. All of these analyses indicate that unless uranium and thorium impurities can be kept to very low levels, probably less than 0.2 ppm, the irradiated metal will have more than 10 nCi/g of transuranic contamination, which would have to be removed by a volume process such as melting to achieve TRU decontamination.

TABLE 2. Calculated (ORIGEN Code) and Analyzed Significant TRU Elements in Base Metal of Two PWR Fuel Hulls

	PWR-1		PWR-2	
	Predicted (nCi/g)	Found (nCi/g)	Predicted (nCi/g)	Found (nCi/g)
^{238}Pu	2.5	2.7	0.46	0.63
^{239}Pu	0.35	0.49	2.6	2.8
^{240}Pu	0.44	0.69	0.94	1.4
^{241}Pu	167	250	104	200
^{242}Pu	5.7^{-3}	6.5^{-3}	4.5^{-4}	7.1^{-4}
^{241}Am	0.60	1.0	2.6	3.0
^{243}Am	0.16	6.4^{-2}	2.1^{-3}	--
^{242}Cm	16	9.4	1.3^{-2}	1.9^{-2}
^{244}Cm	49	10	5.8^{-2}	7.9^{-2}

The analyses of the hulls have shown that about half of the transuranic activity could be removed by leaching. The removal of the remaining half will require removal of the surface oxide layer. A process which will remove the oxide layer from Zircaloy without severe corrosion of the underlying metal is necessary if Zircaloy containing less than 10 nCi/g TRU is to be recovered. The removal of transuranic elements in the metal will only be achieved by zone refinement during melting, by melt-slag interactions, or by reduction of allowable uranium and thorium impurities in the original Zircaloy tubing.

The comparison of the analytical results with other reported data show a modest but explainable difference. Jenkins and Taylor (1977) described some hulls after leaching in nitric acid in a standard manner at Karlsruhe as containing 9 to 17 $\mu\text{g/g}$ of ^{239}Pu and 0.7 to 2.4 mCi/m^2 of internal surface area. This compares with 0.4 to 9 $\mu\text{g/g}$ found for BWR and PWR-1 samples in Table 1. The same two samples show levels of 0.2 and 2.3 mCi/m^2 of internal surface area. The exposure of the BWR piece is the most comparative, about 24,000 MWD/T. PWR-2 was a mixed oxide element and thus is technically biased to higher Pu content (18 $\mu\text{g/g}$ and 8.9 nCi/m^2). PWR-1 has substantially higher exposure.

Jenkins and Taylor also found 30 to 50% of the alpha activity could be removed by ultrasonic leaching in various solutions and that the alpha activity was less than 2 μm into the surface. These observations do not conflict with our finding in Table 1. Their report of associated gamma activity showing ^{106}Ru , ^{144}Ce , ^{125}Sb , ^{124}Cs , ^{137}Cs , ^{60}Co , and ^{54}Mn reached in that order when corrected to reactor discharge compares to our ^{134}Cs , ^{106}Ru , ^{137}Cs , ^{144}Ce , ^{125}Sb , ^{54}Mn , ^{60}Co ranking. However, their values are two to three orders of magnitude larger than ours. This large difference probably arises from the different leaching conditions.

SUMMARY

The zirconium alloy portion of the fuel hulls is a low density metallic waste with a surface to mass ratio of 4 to 5 cm^2/g . Half of this surface (outside) area is coated by a 10 to 100 μm adherent layer of ZrO_2 overlaid

by a variable layer of $(\text{Fe, Ni, Cr})\text{O}_x$ (crud) generally about 4 to 5 mg/cm^2 . The other half of the surface area (inside) is coated by a thin ($<10\ \mu\text{m}$) ZrO_2 layer with about 0.01% adherent fuel. There is a small area of scratches, cuts, etc., exposing bare metal.

About half of the adherent fuel can be leached from the surface with various decontaminants. The remaining half requires quantitative removal of the zirconium oxide corrosion product layer in order to remove the fuel. The residual metal contains transuranic elements originating from irradiation of impurity uranium and thorium in the Zircaloy. In order to be less than 10 nCi/g after a normal exposure, the original concentrations must be much less than the ASTM allowable 3 ppm uranium, probably $<0.2\ \text{ppm}$.

PROCESS SELECTION

Initial feasibility studies (Griggs 1974) had indicated that the removal of the zirconium oxide corrosion layers from the zirconium alloy metal would be necessary to achieve satisfactory decontamination levels. Two methods were indicated as potentially useful: (1) hot anhydrous HF and (2) a fused anhydrous fluoride salt. Parameters of both of these methods were tested in the laboratory on both autoclaved and irradiated Zircaloy tubing. The most promising method -- hot, dry HF followed by an aqueous strip -- was scaled up into a batch process that treated about 50 g/batch. The subsequent scaleup into kilogram size is currently being tested.

INITIAL STUDIES--GAS REACTIONS

Exploration of gaseous and fused salt stripping methods was conducted in a apparatus shown in Figure 3. One-half inch samples of autoclaved and/or bare Zircaloy tubing were treated in this device in order to develop time-temperature-concentration information. The sample holder shown in Figure 3 served as an accurate temperature measurement and sample withdrawal mechanism. Pieces of Zircaloy fuel tubing one-half to one inch long were slipped over the holder so the spring of the thermocouple pressed the sensitive tip to interior surface of the tubing, thus holding the tubing in place and accurately measuring its temperature at the same time. The sample thus mounted was placed in the top portion of the entrance tube and the top fitting closed around the thermocouple sheathing with a split wedge of polytetrafluorethylene which was tightened after the chamber was flushed with argon. The treatment sequence involved opening the ball valve and lowering the sample to the heated portion of the vessel for a specific treatment time. The sample was then raised to the top of the vessel, cooled, and withdrawn through the ball valve for removal.

FIGURE 3. Apparatus for Treating Samples in Gaseous HF or Fused Fluoride Salts at Elevated Temperatures

Samples of Zircaloy-2 fuel tubing were autoclaved in water at 360°C-3000 psi for 1546 and 3446 hours, producing weight gains of 35 and 47 mg/dm², respectively. Samples of this oxidized tubing were subjected to various concentrations of HF in argon at various temperatures between 530 and 620°C for various times. It was found that the lighter oxide could be made removable by treatment in 5% HF at 580°C for 20 minutes, while the heavier oxide required 15 minutes in 100% HF at 590°C. Further experimentation showed that 50 to 75% HF in argon at 600°C for one-half to one hour gave the best treatment for subsequent removal of the anticipated oxide layers in an aqueous solution.

The mechanism of the gas-solid reaction was briefly explored by treating unoxidized Zircaloy at 500, 550, and 600°C in 50% HF-50% Ar for various times. The weight gains of these samples versus time is shown in Figure 4. This figure shows that the reaction rate of HF with Zircaloy increases with decreasing temperature from 600 to 500°C. Inasmuch as the reaction of HF with zirconium dioxide is slow in this temperature range (Slotnick 1964) and the fact that treatment of oxidized zirconium in HF at 550 to 650°C produce removable films suggests the 550 to 650°C temperature is necessary to produce film imperfections allowing the gas to react with the metal. This view was further substantiated by examining metallographically one of the 47 mg/dm² oxide specimens after 4-1/2 minutes in 600°C HF. The section of

FIGURE 4. HF-Zr-2 Reaction 50% HF, 50% Argon

the reacting surface is shown in Figure 5. Examination of the section in a microprobe showed that the dark reaction product between the metal and the oxide layer was substantially fluoride and zirconium, as seen in Figure 6. X-ray diffraction showed a pattern corresponding to ASTM Card Number 20-1471 ($\text{ZrO}_{0.44}\text{F}_{3.12}$).

FIGURE 5. Metallurgical Section of a Piece of Oxidized (47 mg/dm^2) Zircaloy Treated for 5 Minutes in HF-Ar Mixture at 600°C (Note oxide layer being separated from metal by dark material- see Figure 6)

The proposed mechanism of heat caused imperfections in the corrosion product oxide at 600°C that could result from differential thermal expansion coefficient for the metal and oxide. An observation bearing on this hypothesis is that when a partially treated piece is stripped in the aqueous solution, the oxide layer on the inside of the tubing is the hardest to remove. It was found in early runs that the outside oxide layer was completely removed while the inside layer was nearly intact. Literature values of the thermal expansion coefficient for the metal and monoclinic oxide are very similar. This does not confirm or deny this mechanism. The difficulty of removing the internal oxide on a piece of tubing is not a practical problem because in actual fuel hulls the internal oxide is much thinner than the external oxide.

FIGURE 6. SEM Examination of Sample Similar to the One Shown in Figure 5 (Note material between oxide and metal shows high in F)

The weight gains during fluorination were measured during the initial studies and it was found that samples with light oxide layers would completely strip in subsequent aqueous treatment at weight gains of a few hundred mg/dm^2 . Heavy oxide layers required more reaction for complete stripping. Treatment in 50 to 75% HF at 600°C for 45 minutes to one hour produced weight gains of about $700 \text{ mg}/\text{dm}^2$ and modified films on most specimens that could be subsequently stripped.

The reactions involved in the film modifications process are believed to include all of the following to different degrees:

Reaction 1 is believed to be the principal reaction. Reactions 2 and 3 are considered small side reactions and reactions 4, 5, and 6 are detrimental

corrosion reactions. The extent reactions 4, 5, and 6 can proceed is determined by the sweep of the H_2 and H_2O out of the reaction area by the argon carrier gas. As determined subsequently, reactions 5 and 6 can proceed rapidly if an argon sweep flow is not maintained. The presence of H_2O is severely corrosive to the zirconium metal.

Fluoride bearing gases other than HF were briefly tested for applicability. The gases tested were as follows:

<u>Gas</u>	<u>Temperature</u>	<u>Result</u>
CCl_2F_2	$570^{\circ}C$	Severe pitting and distortion at scratches and cut ends.
CF_4	550, 600, $650^{\circ}C$	No reaction even with bare Zircaloy.
BF_3	500, 560, $600^{\circ}C$	Exothermic reactions, weight gains 40-150 $mg/dm^2/min$.

Comparison of these runs to the HF treatment shows its superiority. No further gas reactions were explored.

In summary, preliminary studies indicated a gas-metal reaction takes place on oxidized Zircaloy at $600^{\circ}C \pm 50^{\circ}C$ by HF penetration of imperfections thermally produced in the protective corrosion product layer. A soluble sublayer of ZrF_4 is produced that detaches the zirconium oxide from its metal substrate. Several side reactions take place but are controllable. A uniformly attacked Zircaloy piece with about 1 mil converted to ZrF_4 is produced during the treatment.

INITIAL STUDIES--FUSED SALT REACTIONS

An alternative (Griggs 1974) to the gas-phase treatment process was treatment in a fused salt bath. The salt selected for testing was a mixture of 37 mole% LiF-37 mole% NaF-26 mole% ZrF_4 , a mixture which had been previously examined for the fluoride volatility process (Miller, Stephan, Boyd, Stieglmeyer 1964) treatment of metal fuel. The salt mixture was prepared from commercial salts, melted at $700^{\circ}C$ in the apparatus shown in Figure 3, and sparged with HF to remove any oxide impurities. Samples of

oxidized and bare Zircaloy tubing were introduced and removed in the same manner (Figure 3) that they had been in the gas phase work. The residual salt on the piece was removed by an aqueous treatment, the same as used in the gas phase treatment. Results of the exploratory runs are shown in Tables 3 and 4.

TABLE 3. Corrosion of Autoclaved^(a) Zircaloy-2 Samples by Treatment in 37 mole % LiF-37 mole % NaF-26 mole % ZrF₄ Salt at Various Temperatures and Times

Sample No.	Salt Temp. °C	Immersion Time	HF Sparge	Metal Loss mg/dm ²	Metal Loss μm
-	695	1 min.	No	3,300	50
J	695	2 min.	Yes	3,890	59
D	700	3 min.	No	5,878	90
H	670 - 680	5 min.	No	9,099	139
I	720 - 740	5 min.	No	9,652	147
C	710	5.5 min.	Yes	11,196	171
F	680 - 690	5.5 min.	Yes	10,976	168
G	680 - 690	5.5 min.	Yes	10,135	155
B	660	20 min.	No	10,184	155

(a) Weight gain during autoclaving averaged 47 mg/dm²

Several preliminary conclusions can be drawn from Tables 3 and 4 and other studies:

1. corrosion occurred mostly in the first 5 min.,
2. the amount of adhering salt was excessive and roughly proportional to the corrosion, and
3. the corrosion and corrosion rates were excessive and much higher than previously reported values (Miller, Stephan, Boyd, Stiegelmeier 1964).

Because excessive corrosion and adhering salt represented an undesirable side stream, fused salt treatment was investigated to determine if the side stream

TABLE 4. Salt Adhering to Tubing Samples When Removed From Corrosion Tests (Shown in Table 3)

Sample No.	Corrosion μm	Sample Weight Before Cleaning g	Sample Weight After Cleaning g	Weight of Adherent Salt g
-	50	2.5223	1.5791	0.9432
J	59	2.6340	1.5811	1.0529
D	90	2.1794	1.4211	0.7583
H	139	2.5250	1.1493	1.3757
I	147	1.9819	1.1073	0.8746
C	171	2.0973	0.9817	1.1156
F	168	2.9630	0.9397	2.0233
G	155	2.6470	1.0156	1.6314
B	155	2.9406	1.0522	1.8884

could be reduced to acceptable levels. This investigation was conducted by P. C. Burrier, D. C. Drennen, and E. S. Bartlett of the Battelle-Columbus Laboratories in 1975 on a subcontract (earlier work (Miller, Stephan, Boyd, Stiegelmeier 1964) of BCL was done on this fused salt bath. Their investigations are summarized below).

The corrosion of plain and oxidized Zircaloy-2 was tested in a molten salt bath of 37 mole% NaF, 37 mole% LiF, 26 mole% ZrF_4 at 704°C . The effect of hafnium contamination ($\sim 3\%$) of the zirconium fluoride, time, hydrogen fluoride sparge, and surface oxide on the Zircaloy were examined. It was found that the corrosion rate was nearly parabolic without the HF sparge and was relatively unaffected by an oxidized surface layer ($\sim 83 \text{ mg/dm}^2/\text{wt}$ gain from autoclaving). Sparging with HF increases the corrosion rate substantially and produces nearly linear dissolution kinetics. The presence of hafnium impurity in ZrF_4 caused a two- to three-fold increase in corrosion rate. The salt adhering to the removed specimen was nearly proportional to

the Zr corrosion. Because of differences in temperature or equipment, it is difficult to compare the rates on a quantitative basis. However, Miller et al. (1964) achieved rates of 21 to 58 $\mu\text{m/hr}$ on Zr-2 at 650°C with HF sparge. Table 3 indicates rates of about 30 $\mu\text{m/min}$ on Zr-2 at about 700°C with/without an HF sparge, while this work gave rates of 7 to 12 $\mu\text{m/min}$ on Zr-2 at 704°C.

In attempts to achieve lower dragout losses, later work at Battelle-Columbus Laboratories by D. C. Drennen, E. S. Bartlett, and J. B. Hallowell in 1976 has explored the possibility that salt mixtures with lower viscosity would prevent or minimize formation of a zirconium-enriched, frozen salt "cocoon" around the Zircaloy hulls. It was also of interest "to hold the rate of attack or corrosion to a relatively low value to achieve a rate of metal removal compatible with large-scale processing." Additions of zirconium oxide were studied to simulate the effects of bath aging on dragout and corrosion rate. This work is summarized below.

1. Specimens were exposed in a salt with the lower melting point than that previously used. This salt composition, in mole percent, was 38NaF-24LiF-38ZrF₄. It had a reported melting point of 450°C.
2. The baseline salt bath, 37NaF-37LiF-26ZrF₄, was sparged with BF₃ to promote possible formation of complex alkali-borofluoride mixtures with reduced viscosity.
3. Additions of zirconium oxide were made to the baseline salt bath to determine the extent to which corrosion rate would be reduced; the effect on salt-dragout was also determined.

The equipment included a nickel crucible to contain the fused salt, a surrounding graphite chamber to contain a controlled (argon) atmosphere, a furnace to maintain the chamber at the desired temperature, and supplies of argon and BF₃ gases with an appropriate gas-drying train.

A 100-ml nickel crucible was used with a capacity of about 250 and 290 g of molten salt No. 1 and No. 2 respectively. The two compositions of salt were used, in mole percent:

1. 37NaF-37LiF-26ZrF₄ (melting point 600°C)
2. 38NaF-24LiF-38ZrF₄ (melting point 450°C)

All ZrF_4 used in salt mixtures was of the low-hafnium grade, with a specified maximum of 0.017% hafnium. The salt bath was operated at 704°C (1300°F). Samples of Zircaloy tube remaining from the 1975 studies were immersed in the salt for periods of 1, 10, 30, or 60 min.

Unoxidized samples of Zircaloy-2 tube and samples which had been oxidized by autoclaving (to produce an oxidation weight gain of 40 to 60 mg/dm^2) at Pacific Northwest Laboratory were used. The unoxidized specimens were 1.45 cm OD by 1.28 cm ID by nominally 2.54 cm long. After exposure, the samples were weighed to determine the gross weight of the tube with adhering salt, then cleaned to remove salt in a boiling aqueous solution containing 2-1/2 wt% ammonium oxalate. The samples were then rinsed thoroughly, dried at 104°C (220°F), and weighed to determine metal loss. Some representative samples were metallographically examined and analyzed by a electron microprobe to determine sodium and zirconium gradients in the adhering salt.

Based on the work done to date, the following conclusions were drawn:

1. The addition of up to 15 wt% (7.7 mole %) of zirconia to a "baseline" salt composition resulted in modestly decreased corrosion rates with a slight decrease in salt dragout.
2. The use of a salt composition (No. 2) with a melting point and, presumably, a viscosity lower than that of the "baseline" salt resulted in decreased corrosion attack, anomalous corrosion behavior (i.e., essentially no increase in weight loss with exposure time), and reduced salt dragout. Corrosion and dragout behavior were dependent on the age of the bath.
3. The use of the BF_3 sparge with the "baseline" salt resulted in increased corrosion rates, but generally lower dragout values that decreased with sample exposure times greater than 30 min and/or with bath aging.
4. The specific salt dragout and weight loss of unoxidized and oxidized Zircaloy-2 samples after exposure in Salt No. 2 (in mole percent, $24\text{LiF}-38\text{NaF}-38\text{ZrF}_4$) were identical.

5. The Zircaloy-2 samples exposed to Salt No. 1 with and without a BF_3 sparge were corroded in an intergranular manner.
6. Both cocoon formation and viscosity of the fused salt are important to dragout losses.

Review of this and our previous work on fused fluoride salt removal of zirconium oxide layers from zirconium alloys showed the approach was less desirable than the gas-aqueous process. The three principal defects were (1) the substantial corrosion of the metal, (2) the substantial secondary waste generation (salt dragout), and (3) the difficult handling condition (anhydrous and anaerobic). No further work was done on this process.

In summary, tests of several fused fluoride salt mixtures showed they were capable of removing the zirconium oxide film at about 700°C ; however, they all corroded metal more rapidly than desired and produced more difficult to recycle secondary waste than desirable. Attempts to reduce corrosion were not successful enough to qualify the fused fluoride salt process for further development.

INITIAL STUDIES--AQUEOUS STRIP

The removal of the zirconium oxide corrosion films from Zircaloy by aqueous treatment is possible only with very thin films and fluoride solutions. If the film is not penetrated in a fairly uniform manner, the localized corrosion of the exposed metal becomes severe before all the film is removed. Treatment in high temperature (600°C) fluoride produces a water soluble fluoride film allowing removal by aqueous processes.

Initial experiments with samples employed the decontamination solution developed by Meservey (1970), which was reported to be able to remove some zirconium oxide from zirconium. Actually the solution would only remove layers too thin to be of practical interest for this task. The solution

0.4 M ammonium oxalate
0.16 M ammonium citrate
0.1 M ammonium fluoride
0.3 M hydrogen peroxide
pH 5 95°C

proved to be quite effective in removing the oxide modified by the fluoride gas treatment and was used in initial work to optimize the gas treatment process. Subsequent tests with autoclaved (47 mg/dm^2) and bare samples which had been treated for 20 to 30 minutes at 600°C in HF-Ar indicated that reducing the pH of the strip solution to 4, raising the fluoride to 1 M, or reducing the H_2O_2 concentration to zero caused the metal corrosion rate to increase substantially without a compensating increase in the zirconium oxide removal rate. Lowering the normally 0.3 M H_2O_2 to 0.1 M or substituting the ammonium citrate by an equimolar concentration of Na_2 EDTA did not affect the stripping operation significantly. The original solution was continued in use for the development studies.

In summary, variations on the originally formulated solution composition did not improve its function, and some variations made it worse. No further development was done. However the precipitation of ammonium oxalate from the solution at room temperature could probably be eliminated without reducing the solution effectiveness.

RADIOACTIVE TESTS

The determination of an effective process for removing zirconium oxide from autoclaved Zircaloy tubing was followed by a test on two pieces of fuel cladding. In order to confine the radioactivity to a small inexpensive system, the test was conducted in a heated piece of 1.9 cm (3/4-in.) stainless steel tubing closed with a Swageloc fitting on each end. Diagram of the test setups are shown in Figures 7 and 8. The test sample was loaded into the tubing in a glove box and after the test the joining 3.2 mm (1/8-in.) stainless steel tubing was clipped with cutters to seal it and transferred back into the glove box for unloading.

The first piece tested was the residue of the Saxton cladding used for previously described analysis. The 1.3 cm long piece of tubing was abraded on one end for 0.6 cm thus giving a mix of bare and oxidized Zircaloy which was treated at 600°C for 30 minutes in a 50% HF-50% Ar gas. This treatment produced a weight gain of 286 mg/dm_2 and was followed by 1.2 hours in the

* INDICATES THE RATIO ACTIVITY OF THE UNIT AFTER THE RUN AND DISASSEMBLY WITH A GAMMA SCANNING INSTRUMENT IN COUNTS/MINUTE

FIGURE 7. Experimental Setup for Treating Saxton Hull in 600°C HF

*INDICATES READINGS ON A C. P. IN mR/hr AFTER RUN AND DISASSEMBLY

FIGURE 8. Experimental Setup for Treating PWR-1 Hull in 600°C HF

aqueous baths containing 0.4 M ammonium oxalate, 0.16 M ammonium citrate, 0.1 M ammonium fluoride, and 0.3 M hydrogen peroxide at 95°C and pH 5. The total weight loss was 3.6 g/dm² (~2.3 mils) for the whole process. The piece appeared completely stripped except for two or three islands <1 mm². Analyses of strip solutions and cleaned metal showed removed surface alpha activity of 955 nCi/cm² ID oxide area and cleaned metal alpha activity of 3.4 nCi/cm² ID area for a decontamination factor of 280. However, the metal volume contained 3.1 nCi/cm² that was not available to a surface process. Excluding this, the DF would be about 3200.

The second piece was a 2.5 cm piece of high exposure PWR Zircaloy fuel cladding which was stripped chemically to evaluate the decontaminating process. The piece of cladding had been leached in a nitric acid fuel dissolving operating and rinsed with dilute nitric acid. The piece was weighed, then treated in a slow flow of argon and HF (about 50% HF) at 595 to 625°C for 45 minutes. The treated piece was immersed in a 0.4 M ammonium oxalate, 0.16 M ammonium citrate, 0.1 M ammonium fluoride, 0.3 M hydrogen peroxide solution for 45 minutes at 90 to 95°C. This process removed all of the visual oxide from the surface except for two (<1 mm dia.) spots. An additional 45 minute treatment did not improve its visual appearance, shown in Figure 9.

FIGURE 9. PWR-1 Hull After Treatment in 600°C HF and Aqueous Strip

Weight loss from the combined treatments corresponded to 3.2 g/dm^2 or 0.05 mm. The first aqueous stripping solution was decanted in order to apply a more concentrated HF solution to completely dissolve the fine black solid for analyses. These solutions and a solution of dissolved metal were analyzed for total alpha count to determine the degree of decontamination achieved. The decontamination factor was about 1220 with a substantial portion of the residual alpha activity originating in the base metal from irradiation of uranium impurity, which is not available to surface decontamination. The residual alpha count in the base metal after surface decontamination was 24 nCi/g. Table 5 summarizes the results.

TABLE 5. Decontamination of PWR Clad Hulls in HF-Ar (600°C) Followed by an Aqueous Strip

	<u>Activity Recovered</u>	<u>Activity in Residual Hull</u>	<u>DF</u>
PWR-1	10^4 nCi/cm^2	8.2 nCi/cm^2	1220
PWR-2	10^3 nCi/cm^2	3.4 nCi/cm^2	280

The radioactive distribution in the equipment, traps, and filters was of interest for the scaleup design. Referring to Figures 7 and 8, the gamma readings taken with a hand-held radiation probe after disassembly are shown. No trap showed a particular ability to remove the activity except by filtration. The activity is probably a very fine particulate which can move effectively through the system at very slow gas velocities. In Figure 7, the gas velocity was only about 1 cm/min in the flasks above the solution and it still carried to the last flask, which had a modest filtering ability. Similarly, in Figure 8, the gas velocity in the unfilled traps (3/4-in. tubing) was ~ 10 cm/min and still the activity was only removed by filtering capacity. No attempts were made to trace the small amount of ^3H through the system.

In summary, the test of the HF-Ar plus aqueous strip process on irradiated material showed excellent decontamination for TRU elements and zirconium oxide. The irradiated pieces cleaned up better than the autoclaved Zircaloy tubing used for development. This is to be expected because the irradiated oxide coating contains more flaws than the autoclaved Zircaloy tubing. It appears surface DFs of 10^3 to 10^4 can be expected with this process. The volumetric contamination of the metal is not affected by this surface cleaning.

EQUIPMENT DESIGN

The scaleup of the single-sample experiments described above into experiments of ten to thirty samples took place at a time when many of the process variables had not yet been optimized. The equipment was designed to allow flexibility in as many operations as possible. Flow through the gas reaction vessel may be either from top to bottom or bottom to top depending upon the requirements of the experiment. Aqueous washing may take place in either or both of the vessels depending upon need or circumstances. The system also has the ability to use pure HF, Ar, or other gases in the reaction vessel and to mix them to any desired proportion. That portion of the system designed to remove the HF, H₂O, and particulate matter from the off-gas stream may also be bypassed or added to as necessary to achieve flexibility. Once the system was installed in the cave and radioactive materials processed, change would be much more difficult. Replacement of items will be required from time to time and every effort was made to design access to each by use of the manipulators. Gravity flow to a few low drain points was incorporated into the system to insure removal of all residual liquid after the aqueous wash and allow ease in drying to lessen corrosion and attack of the Zircaloy by HF during the next gas treatment phase. Diagrams of the gas and aqueous treatment vessel, condenser, and gas scrubber assembly are shown in Figures 10, 11, and 12 respectively.

MATERIALS SELECTION

Several materials of construction for the system were tested for their resistance to corrosion by the aqueous decontamination solution described previously. The materials corrosion-tested were Hastelloy N, Inconel 600, 304L and 316 stainless steel welded to themselves with the same filler material. Samples of Inconel 600 welded to 316 and 304L stainless steel with Inconel 600 filler were also tested. Each of the materials was tested in the as-welded condition. With the exception of Hastelloy N, all materials appear to be equally corrosion resistant at the end of 400 hours of exposure as shown in Table 6 and Figure 13.

FIGURE 10. Decontamination Vessel

FIGURE 11. HF Condenser

FIGURE 12. Gas Scrubber System

TABLE 6. Weight Loss of Specimens in Decontamination Solution at 90°C

Welded Materials	Weight Loss	
	200 Hours	400 Hours
Hastelloy N - Hastelloy N ^(a)	13738 mg/dm ²	29074 mg/dm ²
Inconel 600 - Inconel 600 ^(b)	24 "	36 "
304L - 304L SS ^(c)	71 "	25 "
316 - 316 SS ^(d)	25 "	33 "
Inconel 600 - 314L SS ^(b)	18 "	30 "
Inconel 600 - 316 SS ^(b)	22 "	32 "

(a) Welded with Hastelloy N Rod

(b) Welded with Inconel 82 Rod

(c) Welded with 308 rod. (The 200-hour exposure sample appeared to have a mottled or burnished surface.)

(d) Welded with 316 rod.

FIGURE 13. Hasteloy N Specimens After Treatment in Aqueous Strip Solution* for 200 Hours at 90°C. *0.4 M ammonium oxalate, 0.16 M ammonium citrate, 0.1 M ammonium fluoride, 0.3 M hydrogen peroxide, pH 5.

Previous operation of the gas treatment vessel constructed of Hastelloy N, stainless steel (304L), and Inconel 600 had shown that stainless steel could not withstand the 600°C HF environment. Inconel and Hastelloy N were resistant to high temperature HF but only the Inconel could withstand both the aqueous decontaminant and the high temperature HF. Thus, the gas treatment vessel was made of Inconel 600 and the balance of the system of 304L and 316L stainless steel and polytetrafluorethylene valve packing.

SYSTEM ASSEMBLY

The system was first set up in a laboratory hood to explore the various operating parameters and perfect the operating technique prior to installing it in a lead cave for shielded remote operation. In general, the assembly had standard stainless steel tubing, fittings, and ball valves with polytetrafluoroethylene seals. The operating experience is subsequently discussed.

The system was disassembled when the pilot testing was over and reinstalled in a shielded facility equipped for remote operation. Views of this cave are shown in Figures 14 and 15. Figure 16 shows the equipment in the cave together with a process diagram. Not shown is a modified hydraulic cable shear for remote chopping of the cladding hulls into one- to two-inch lengths.

FIGURE 14. Cave for Radioactive Work. (Decontamination equipment installed inside.)

FIGURE 15. HF/Ar Supply and Control Equipment

FIGURE 16. Process Equipment Installed in Cave and Flow Diagram
(Note--Flow diagram has the same approximate geometry as picture.)

PROCESS DEVELOPMENT

GENERAL

Previous experimental work to determine the process best suited for hull decontamination had defined some process parameters such as temperature and aqueous strip solution composition. Parameter optimization studies on flow rates, gas mixture ratios, reaction time, and agitation requirements in a reaction vessel containing a number of hulls was required. This work was done using the equipment described previously in the Equipment Design section.

The first requirement was to find the time required for the HF to penetrate the zirconium oxide layer to a sufficient degree to allow removal of the oxide. Flow requirements, gas mixtures, and HF utilization were determined concurrently. Agitation of the hulls was also found to play an important role in the complete removal of the oxide layer.

Only two parameters were studied with regards to use of the aqueous strip solution. The first was simply the length of time required to effect the strip. The second process variable was the number of water rinses necessary to remove residual oxide and solution from the hulls. These determinations were easily made and required a minimum of experimental work.

TIME

Very few experimental runs were made using less than one hour of reaction time. These runs (see Table 7) indicated incomplete penetration of the zirconium oxide--zirconium interface, resulting in incomplete stripping of the oxide from the metal. As a measure of the amount of HF that had reacted with the hull material an attempt was made to weigh the hulls following treatment at 600°C. These results were not conclusive or meaningful as the hull oxide layer was rather loosely held in place and much of the material which flaked off the hulls could not be easily recovered.

TABLE 7. Experimental Runs Comparing Reaction Times

<u>Reaction Time</u>	<u>HF Flow Rate cc/min</u>	<u>AR Flow Rate cc/min</u>	<u>Surface Area Oxidized Samples, dm²</u>	<u>Average Weight Loss Oxidized Samples, mg/dm²</u>	<u>Surface Area Unoxidized Samples, dm²</u>	<u>Average Weight Loss Unoxidized Samples, mg/dm²</u>	<u>HF Excess Flow Rate cc/min</u>	<u>% Oxide Film Removed</u>
30	180	0	2.979	1321	0.173	3118	7.3	10
60	180	0	2.859	2752	0.173	3062	31	100
40	80	28	0.507	2641	0.505	2490	--	85
60	80	28	0.662	2204	0.340	2935	14	95

TEMPERATURE

Experimental work done during the process selection portion of this work had determined the gas phase reaction temperature necessary to initiate the HF-Zr reaction through the zirconium oxide layer (i.e., $600 \pm 50^{\circ}\text{C}$).

AGITATION

Agitation of the hulls during HF treatment was required to allow reaction with the entire hull surface. The contact point between hulls in the reaction vessel prevents penetration by the HF, resulting in incomplete oxide removal at contact points. Continuous agitation was not necessary. Some stirring of the sample has been found to be necessary to shift points of contact between the hulls where the oxide layer exposure to the HF is insufficient for complete oxide removal during the aqueous wash.

The effect of stirring was investigated in the 1706-KEL cave facility to guide design effort for the planned rotary HF-reactor. The samples were stirred (1) occasionally, (2) at 1-1/3 revolutions per minute (rpm), and (3) at 4-1/2 rpm while undergoing equal 600°C treatments. Table 8 shows the average specimen weights lost during equal stirring times. The rate increase between occasional stirring and stirring at 1-1/3 rpm was only slight ($\sim 3\%$), while the increase between occasional stirring and stirring at 4-1/2 rpm was about 10%. In general, this modest rate should cause no problems in the rotary HF-reactor.

TABLE 8. Average Specimen Weight Losses for Different Stirring Rates During the Investigation

<u>Stirring Rate</u>	<u>Average Specimen Weight Loss, g/dm^2</u>
Occasionally	2.9 ± 0.1
1-1/3 rpm	3.0 ± 0.1
4-1/2 rpm	3.2 ± 0.1

WASH TIME

A wash time in the decontamination solution of about 30 minute duration at 95°C followed by two rinses in the distilled water was effective in the removal of oxide from the surface of the hull following HF treatment.

GAS MIXTURE AND FLOW RATES

Initial runs were made using about a 50-50 mixture of HF and Ar. The mixture was selected to allow a continuous flow of HF past the hulls and minimize the total HF mass flow while carrying away any gaseous reaction products that may have formed. The approximate velocity of the gas flow past the hulls is indicated in Table 9. The first several experiments indicated an excess HF flow of about 10 cc/min/dm² of Zircaloy surface area (in excess of stoichiometric requirements) passing through the reactor vessel was required to effect 98% removal of the oxide layer (see Table 9). A weight loss of at least 2500 mg/dm² and preferably 3000 mg/dm² following aqueous treatment was also required to assure complete removal of the oxide.

Problems were encountered with the use of undiluted HF. Reaction rates were not always controllable, resulting in temperature excursions within the reaction vessel believed to be the results of hydrogen accumulation during the HF-Zr reaction ($4\text{HF} + \text{Zr} \rightarrow \text{ZrF}_4 + 2\text{H}_2$). The use of argon was found to be necessary to provide a means to control the H₂-Zr reaction and thus the formation of zirconium hydride by diluting the HF and providing a vehicle to carry away the hydrogen as it was formed. Hydriding of the zirconium is not desirable because the hydride becomes extremely brittle, causing it to crumble. The resulting high surface area material is quite pyrophoric and presents a handling and recovery problem. In addition to the use of argon in the gas mixture (three parts HF to one part Ar) to carry away the heat released, it was also determined that the flow of the gas mixture into the bottom of the vessel and out the top was required for effective removal of the hydrogen.

Another problem area to which special attention must be paid during the HF treatment phase is the presence of moisture. Severe corrosion of the hulls was noted during run C-II when the reactor vessel and associated piping were

TABLE 9. Experimental Test Results for Runs of One Hour

Run	HF Flow Rate cc/min.	Ar Flow Rate cc/min.	Total Surface Area Oxidized Samples, dm ²	Average Weight(c) Loss Oxidized Samples, mg/dm ²	Total Surface Area Unoxidized Samples, dm ²	Average Weight(c) Loss Unoxidized Samples, mg/dm ²	Gas Mixture Velocity in Reactor Vessel cm/min	HF Excess Flow Rate cc/min	% Oxide(c) Removal
I	43	45	1.700	--	--	--	10	--	Incomplete
II	43	50	0.851	984	0.895	2678	11	--	50
III	80	50	0.852	2438	0.909	3304	15	--	70
v(a)	40	25	0.675	1180	0.342	2103	8.0	6	40
VI	80	25	0.662	2204	0.340	2935	12	14	95
VII	35	70	0.720	595	0.327	1660	12	9	60
IX	80	0	2.855	2176	0.336	2422	9	6	70
X	180	0	2.696	2832	0.226	3238	21	30	99
XI	180	0	Reaction uncontrolled				21	--	--
XII	180	0	2.859	2757	0.172	3062	21	31	100
XIII	180	0	2.979	1321	0.173	3118	21	7.3	10
XIV	100	(100 of H ₂)	Samples badly hydrided				24	--	--
xv(a)	80	25	0.839	2631	0.170	2995	12	27	98
xvi(a)	80	(80 of H ₂)	0.820	2543	0.170	3110	19	26.7	95
xvii(a)	40	25	0.804	1876	0.169	3161	8	10.6	50
C-I(a)	75	25	0.793	2531	0.335	2540	12	--	100
C-II(a)	75	25	Samples had corroded due to moisture						
C-III(a)	75	25	0.734	2823	0.340	2324	12	--	~90
C-IV(a)	75	25	0.670	2811	0.337	2830	12	--	100
C-V(a)	150	50	1.732	4534	0.336	4118	24	--	>99
C-VI(a)	200	67	3.307	3208	0.676	3130	32	--	88
C-VII(a)	200	67	2.452	2866	0.825	3171	32	--	98
C-VIII(a)	200	67	2.408	2998	0.828	3288	32	--	98
C-IX(a)	200	67	2.227	3036	0.8150	3973	32	--	100
C-X(a)	200	67	2.449	3042	0.8160	3954	32	--	100
C-XI(b)	150	50	1.7121	2927	0.4054	--	24	--	100
C-XII(b)	150	50	1.4487	3486	0.4465	3271	24	--	100

(a) Bottom to top flow

(b) Contained irradiated samples

(c) Changes after aqueous strip

incompletely dried from the previous aqueous treatment. Sufficient removal of moisture was found to be possible by the heating of the reactor vessel and piping while purging with argon for about one hour.

TESTS WITH RADIOACTIVE SPECIMENS

Tests were conducted with actual fuel cladding from the BWR material previously described. Tests were planned with PWR hulls but they were not available when the program was active.

Several pieces of irradiated BWR cladding were treated to determine the effect of irradiation on the behavior of the cladding during decontamination. The irradiated pieces of BWR cladding were leached, after mechanical fuel removal, in 95°C 8 M HNO_3 for two 4-hour periods followed by a short, hot, nitric acid rinse. This leach removed most of the leachable fuel from the Zircaloy surface, 0.4 mg/dm² of ^{137}Cs and 7 $\mu\text{g/dm}^2$ ^{60}Co . The leached pieces of cladding about 10 cm long were found to read between 300 and 1200 mR on a closed window CP at contact.

Two oxide removal tests were run using the available irradiated BWR cladding. The cladding was first cut into about 3.3 cm pieces using remote shears. The pieces were then combined with nonirradiated oxidized tubing pieces and treated in 75% HF-25% Ar gas mixture at 600°C for 1 hour (see Table 9). The cooled pieces were then treated in 0.4 M ammonium oxalate-0.16 M ammonium citrate-0.1 M ammonium fluoride-0.3 M hydrogen peroxide solution at 95°C for 30 minutes, rinsed in H_2O for 5 minutes, and the process repeated with clean solution.

The results of both experimental tests (see Table 9) showed the following:

1. Nonirradiated pieces picked up ~10% of the beta-gamma contamination on their surfaces.
2. Surface oxides were completely removed from irradiated and nonirradiated pieces.
3. Irradiated and nonirradiated samples lost 2.9 g/dm² on the first test and 3.8 and 2.9 g/dm² respectively on the second test.

4. Some fine undissolved solids were present in the wash solutions; these can mostly be dissolved in concentrated HF made slightly oxidizing with HNO_3 .

These results are in general agreement with previous tests on oxidized cladding (see Table 9). Decontamination and other secondary waste stream treatments were not quantitatively evaluated.

SUMMARY

Use of excess HF flow, flow from bottom to top, a mixture of HF and Ar, one-hour reaction time, agitation of the samples, and 600°C reaction temperature, resulted in essentially 100% removal of the oxide film from the Zircaloy hull material during the aqueous treatment process. These are the conditions used during treatment of the irradiated hulls.

CONCLUSIONS

The chemical removal of transuranic surface contamination from cladding hulls can be accomplished by treatment in 600°C HF followed by a dilute aqueous strip or a treatment in molten fluoride salts followed by aqueous salt removal. The following general conclusions were drawn about the processes:

1. The treatment of Zircaloy hulls for 3/4 to 1 hour in 600°C $\pm$ 50°C HF-Ar mixture conditions the oxide surface layer for subsequent aqueous removal with total corrosion of 25 to 50 μ m (1 to 2 mils).
2. Several variations of aqueous solutions were no better for the treated film removal than 0.4 M ammonium oxalate-0.16 M ammonium citrate-0.1 M ammonium fluoride-0.3 M hydrogen peroxide at pH 5. Dilution to make ammonium oxalate completely soluble at room temperature appears desirable for some applications.
3. Complete removal of Zircaloy corrosion layers with less than 0.005 cm metal removal is possible.
4. The several fused salt process modifications investigated rapidly remove zirconium oxide corrosion layers but are undesirably corrosive to the metal and produce too large a secondary waste stream by salt adherence to the high surface area pieces.
5. More than 10 nCi/g of transuranic contamination is produced throughout the metal by irradiation of uranium and thorium impurities in the Zircaloy. Removal of this material by volume processes was not investigated but might be accomplished by the fluxed melting in the "Inductoslag" process.
6. The removal of all surface oxide from Zircaloy fuel hulls is necessary for surface TRU element decontamination.
7. The removal of all surface oxide from Zircaloy is necessary if good metallic properties are required from the subsequently melted hulls.
8. All secondary wastes from this process except zirconium, ZrO₂, and other metal oxides can be made volatile for waste treatment densification.
9. Small batch operations were successfully operated remotely.

ACKNOWLEDGMENTS

The help of several people in conducting these experiments is gratefully acknowledged by the authors. In particular, Mr. D. B. Mackey and Mr. N. D. Stice for construction and operation of laboratory setups, Mr. R. G. Moles for cave equipment design, and Mr. J. M. Kelley for radiochemical analyses.

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