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## MANAGEMENT OF WASTE CLADDING HULLS.

### PART II.

## AN ASSESSMENT OF ZIRCONIUM PYROPHORICITY AND RECOMMENDATIONS FOR HANDLING WASTE HULLS

by

B. J. Kullen, N. M. Levitz,  
and M. J. Steindler

MASTER



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ABSTRACT

This report reviews experience and research related to the pyrophoricity of zirconium and zirconium alloys. The results of recent investigations of the behavior of Zircaloy and some observations of industrial handling and treatment of Zircaloy tubing and scrap are also discussed. A model for the management of waste Zircaloy cladding hulls from light water reactor fuel reprocessing is offered, based on an evaluation of the reviewed information. It is concluded that waste Zircaloy cladding hulls do not constitute a pyrophoric hazard if, following the model flow sheet, finely divided metal is oxidized during the management procedure. Steps alternative to the model are described which yield zirconium in deactivated form and also accomplish varying degrees of transuranic decontamination. Information collected into appendixes is (1) a collation of zirconium pyrophoricity data from the literature, (2) calculated radioactivity contents in Zircaloy cladding hulls from spent LWR fuels, and (3) results of a laboratory study on volatilization of zirconium from Zircaloy using HCl or Cl<sub>2</sub>.

I. INTRODUCTION

Management of radioactive waste must ensure protection of the public by (1) providing adequate barriers between the radioactive material and the biosphere and (2) developing waste forms that are compatible with the barriers and that will pose no immediate hazard to the biosphere in the event that barriers are breached. An identification of effective management procedures is possible only when the forms and chemical properties of a given waste material are well characterized. The present study concerns an analysis of the behavior of the zirconium-based metal waste produced in the chop-leach\* head-end step during the reprocessing of commercial light-water-cooled power reactor (LWR) fuel.

\*Chop-leach is the commonly applied head-end process step in which LWR fuel elements are sheared into short segments that have oxidic fuel exposed at the ends. When treated with nitric acid, the oxidic fuel is dissolved, leaving the Zircaloy hulls substantially unreacted.

This waste stream consists of short (2 to 8 cm) sections of Zircaloy\* tubing and, depending on reprocessing plant practice, may also contain Inconel spacer grids, stainless steel fuel-assembly end fittings, and small amounts of Zircaloy fines† material. The steel and Inconel represent ~10% of the metallic components, are not contaminated by undissolved fuel, and generally do not pose a pyrophoric or chemical hazard. These alloys do contain significant amounts of neutron activation products and thereby contribute to the radiation hazard from metallic fuel-assembly residues. Henceforth, the term *hulls* is used to describe this waste stream, whether it consists of only the cladding sections or the entire mix of metallic fuel assembly hardware. This metallic waste stream may be difficult to manage because (1) the hulls are contaminated with beta-gamma emitting fission products and neutron activation products as well as long-lived alpha-emitting transuranic nuclides, (2) zirconium has exhibited pyrophoric tendencies in the past, and (3) the stream is a heterogeneous mixture of materials that differ in form and in chemical properties. Because of these factors, special handling and storage techniques will have to be considered. To aid in the development of these techniques, an assessment and evaluation had to be made of available information on the character and properties of hulls and, most importantly, on the mechanisms and implications of zirconium pyrophority.

The objective of presenting information on the pyrophority of zirconium and Zircaloys is to contribute to the resolution of questions regarding the possible hazards, from pyrophority, of handling the hull waste. Unless the metallic form of the material is changed to one of lesser potential energy such as oxide, it is not feasible to provide absolute assurance that reactions will not take place with Zircaloy hulls or fines. Nevertheless, recommendations are provided that will, based on the information assembled herein, reduce the risk of undesired reactions to reasonable proportions without requiring large-scale or complicated chemical conversions.

For the purposes of this analysis, a distinction is made between the Zircaloy cladding from LWR fuel containing ceramic UO<sub>2</sub> and other forms of zirconium such as the U-Zr alloy fuels and special zirconium claddings which have a history of ignition and explosion. The technologies of zirconium and Zircaloys were reviewed--particularly citations on and experience with reactions occurring during manufacture and routine handling. Much of this information has been presented in a previous report [Levitz] that also includes information on the expected composition of hulls waste and on methods proposed for its handling at reprocessing sites. The present report is complementary and is largely confined to the question of safety, from the standpoint of zirconium pyrophority, in the long-term management of waste hulls.

Sources of information included (a) literature published since the mid-1940's, (b) discussions with persons having experience in metal manufacture, scrap handling, fuel fabrication, fuel reprocessing, and safety, (c) plant visits and process observation, and (d) results from a variety of

---

\* Zircaloys are zirconium alloys with small amounts of tin, iron, chromium, and, in some cases, nickel [ASTM].

† In this report, "fines" refer to metal particles physically removed from and of lesser size than the Zircaloy cladding tube segments.

scouting experiments and tests. It will be shown, on the basis of the above information, that hulls and hardware are safe to handle, while zirconium fines, *per se*, remain a potential hazard. Management techniques are cited, however, that mitigate even the fines hazard and illustrate that the possible risk, in terms of pyrophoric behavior, in handling hulls waste can be reduced to an acceptable level.

## II. HISTORICAL BACKGROUND OF THE BASIS FOR CONCERN OVER THE PYROPHORICITY HAZARD

The term pyrophoricity refers to the capability of materials to spontaneously ignite in air or other (usually gaseous) environs. Ignition occurs when the heating rate produced by an exothermic reaction exceeds the combined rates of conductive, convective, and radiative cooling. Concern over the possible pyrophoric behavior of Zircaloy hulls stems specifically from extrapolation of past experience with other forms of zirconium, since no incident has been reported involving pyrophoricity of Zircaloy tubing, *per se*, in the manufacture of tubing or fuel elements, in the reprocessing of LWR oxide fuel, or in the storage of hull waste.

Some of the experience with the pyrophoricity of zirconium is summed up in selected issues of two series of bulletins issued by the Atomic Energy Commission (AEC),\* namely, "Accident and Fire Prevention Information" [AFP-2, -44, -45, -69, -A, -B] and "Serious Accidents" [SA-44, -44A, -50, -84, -274, -298]. The information regarding these incidents is incomplete, particularly with respect to identifying causes and mechanisms and providing accurate information on the nature of the material involved. The events are included in a summary of zirconium pyrophoricity incidents listed in Table 1.

Most frequently, spontaneous ignition and explosions were associated with materials having high specific areas or high surface-to-volume ratios, such as powders, machining turnings, grinding residues, or sponge.<sup>†</sup> Other incidents involved alloys, with zirconium being either a minor or a major constituent [Schultz, Larsen]. In general, the behavior of zirconium and Zircaloys has been similar.

Pyrophoricity hazards for several forms of zirconium metal are shown in Table 2. Although there is considerable scatter in the quoted data, it can be stated conservatively that zirconium particles under  $\sim 60$   $\mu\text{m}$  in diameter can be considered explosive, and particles under  $\sim 1$  mm in diameter can be categorized as a fire hazard. For comparison, crude data on the chopping of unirradiated Zircaloy tubing (Table 3) indicate that  $\sim 3$  wt % of the resulting fines might be less than  $\sim 350$   $\mu\text{m}$  in diameter and  $\sim 24$  wt % less than  $\sim 1.5$  mm in diameter;  $>75$  wt % of the fines may be considered normally safe materials.

\* Reorganized, in part, as the U. S. Energy Research and Development Administration (ERDA).

<sup>†</sup> Sponge is a form of zirconium produced during manufacture by reduction of the tetrachloride to the metal. Zirconium sponge has a high surface area, may contain impurities, and is consolidated to bulk metal by melting.

Table 1. Forms of Zirconium Involved in Pyrophoricity Incidents

Form	Chemical System or Environment	Hazardous Phenomenon	References
• U - 1 to 20% Zr (alloy)	Aqueous HNO <sub>3</sub> (pickling)	Explosion	[Larsen]
• Zr alloyed with other metals, including lead, copper, misch metal <sup>a</sup>	Not Defined	Explosion	[Andersen, AFP-45]
• Zr - 2.5% Nb - steel	Rolling mill, Zr alloy in steel "picture frame," ~1000°C	Formation of Zr-Fe eutectic; liquid metal ignited and burned	[SA-298]
• Zr-Mg-MgCl <sub>2</sub> solid mixture	Water	Explosion (under water)	[AFP-45]
• Zr impellor (welded plates and shafting)	Aqueous HCl	Abnormally high surface activity (sparking, burning)	[AFP-45]
• Scrap, miscellaneous (chips, turnings)	Ambient air, stored in open bins	Ignition	[SA-84]
• Zr chips, scrap	Machining turnings during chopping involving water sprays	Ignition	[Tetz]
• Zr chips	Milling of massive metal w/water coolant	Flash fire over entire surface of chips	[AFP-45]
• Zr sponge	Ambient air	Ignition	[Tetz]
• Scrap powder	Stored in drums for 3-5 years in scrap yard	Explosion	[AFP-44]
• Zr powder	Aqueous H <sub>2</sub> SO <sub>4</sub> -KHSO <sub>4</sub>	Explosion	[AFP-69]
• Zr powder	Ambient air, 3.8-liter can, Zr-16 wt % water	Explosion (upon opening can)	[AFP-44]
• Zr "dust"	Ambient air	Explosion	[AFP-44]

<sup>a</sup>A mixture of the rare earth metals.

Table 2. Zirconium Pyrophoricity Hazard Derived from Industrial Experience

Form	Dimension	Specific Surface Area, cm <sup>2</sup> /g	Surface Area/Volume, cm <sup>-1</sup>	Remarks	Ref.
<b>POWDER</b>					
a. Experience	1-μm dia	9200	60,000	Pyrophoric under ambient conditions	[Littman]
	<10-μm dia	>920	>6,000	Explosive	[Bulmer]
	10-μm dia	920	6,000	Considered borderline between safe and hazardous powder	[Littman]
	<62-μm dia	~150	~970	Explosive	[Allison]
	<850-μm dia	~10	~70	Hazardous fire and explosion risk	[Allison, Bulmer]
	powder with 3 to 16% moisture	-	-	Spontaneous combustion and explosion	[Holt]
b. Derived conservative guides	<60-μm dia			Explosive hazard	
	60-850-μm dia			Fire hazard	
	>850-μm dia			Normally safe	
	3 to 25% moisture content			Explosive hazard	
<b>SHEET</b>					
a. Experience	0.13-mm thick	~30	~190	Easily ignitable	[Allison]
	0.3-mm thick	12.7	82.7	Borderline between safe and hazardous thickness	[Littman]
	0.3-mm thick	12.7	82.7	Combustion self-sustaining	[TID-5365]
	0.8-mm thick <sup>a</sup>	4.7	30.3	No evidence of pyrophoric behavior	[Littman]
b. Derived conservative guides	<0.3-mm thick			Ignitable with flame	
	>0.3-mm thick			Normally safe	
<b>SPONGE</b>					
Experience and guide	-	100	~520	Shows high incidence of pyrophoricity	[Tetz]

<sup>a</sup>Equivalent to LWR cladding wall thickness.

Table 3. Analysis of Zircaloy Fines Produced by Chopping Unirradiated Tubing [Tetz]

U.S. Sieve No.	Particle Size, $\mu\text{m}$	Size Fraction, wt % <sup>a</sup>	Oxygen Content, wt %
+8	+2380	66.3	0.108
+10	+2000	5.8	0.137
+12	+1680	1.5	NA <sup>b</sup>
+14	+1410	2.9	NA
+25	+710	13.5	0.456
+45	+350	7.3	NA
<45	<350	2.7	3.32

<sup>a</sup>Determined from amount retained on each sieve.

<sup>b</sup>NA = not analyzed

For zirconium in sheet form, Table 2 indicated that metal less than 0.3 mm thick is ignitable while metal with greater thickness is normally safe. LWR Zircaloy fuel-cladding thicknesses may range between 0.6 and 0.9 mm. It should be noted that though there has been a comparison of oxidation rates of various binary alloys of zirconium (presented in a later section), no comparison could be found of the pyrophoric characteristics of zirconium and the Zircaloys. It is assumed, for the purposes of this study, that the differences are trivial.

Some of the information shown in Table 2 on the effects of form and size on ignition is in contradiction with the above guidelines for safe particle size and thickness, e.g., "coarse" powders have been reported as being hazardous. Other values, relating zirconium physical form to pyrophoric response, were found to vary in magnitude from one reference to another. This inconsistency of results is not unexpected since different procedures, differing grades and forms of zirconium, and dissimilar conditions were reported as being used in the various tests. As a result, Table 2, quoting the relationships of zirconium form to safety classifications and comparing zirconium dimensions to pyrophoric hazard, contains conflicting data. Hence, the results are treated as a whole and stability conditions are expressed in terms of the most conservative data found in the literature.

Material identified as "massive" by Bulmer is particles retained on a 12-mesh screen (~1.7-mm openings), or sheet, strip, or wire with a minimum thickness/diameter of 0.13-mm or with a minimum cross-sectional area\* of 1.9  $\text{mm}^2$  [Bulmer]. Since the designation "massive" normally applies to nonpyrophoric material, this implies that Zircaloy fines need some special consideration, but the hulls are a massive form and should be safe from ignition hazard. The impact of a fines fire on a mixture of fines and hulls needs separate consideration (see Section IV).

\* Assumed to be across the longitudinal axis of the form.

Factors that appear to contribute to the pyrophoricity of zirconium are listed in Table 4. Relationships between some of these factors have been established, and examples of correlations or relationships reported in the literature include:

- a. ignition temperature as a function of particle diameter and mass of material, assuming spherical particles, as shown in Fig. 1;
- b. ignition temperature of zirconium foils as a linear function of the logarithm of the specific area, as shown in Fig. 2;
- c. ignition at room temperature as a function of foil thickness and high (20 to 50 atm) oxygen pressure, as shown in Table 5 and Fig. 3. Of interest, extrapolation of the curve to 0.2 atm (in ordinary air) gives a value of  $\sim 0.0254$  mm for foil thickness.

Table 4. Apparent Effect of Selected Factors on the Pyrophoricity of Zirconium

Factor	Trend of Factor Tending to Increase Pyrophoricity
Particle Size	Decrease
Surface-to-Volume Ratio <sup>a</sup>	Increase
Specific Surface (area/mass)	Increase
Moisture Content of Environment	3-25% maximizes pyrophoricity as does alternating wet/dry conditions
Temperature	Increase
Total Mass of Zirconium	Increase
Gaseous Environment	Increasing oxidizing power
Impurities, alloying agents	Complex relationship
Energy of Ignition Source	Minimum required for ignition; not directly related to pyrophoricity

<sup>a</sup>Geometry of mass relates to dissipation of heat once reaction has been initiated. The surface-to-volume ratio refers to the individual particles or pieces of the zirconium mass.

The correlation from Fig. 1 indicates that sheet zirconium equivalent to hulls (see Table 2) would have a calculated ignition temperature of about 930°C. Recent tests [Steindler], however, indicate no ignition at temperatures up to 1600°C in air.

Historically, the frequency of ignition/explosion incidents involving zirconium declined with increased experience. Improvements in the manufacturing process, giving a higher purity product, contributed to this decline. Safe procedures in the handling of even micron-size powder

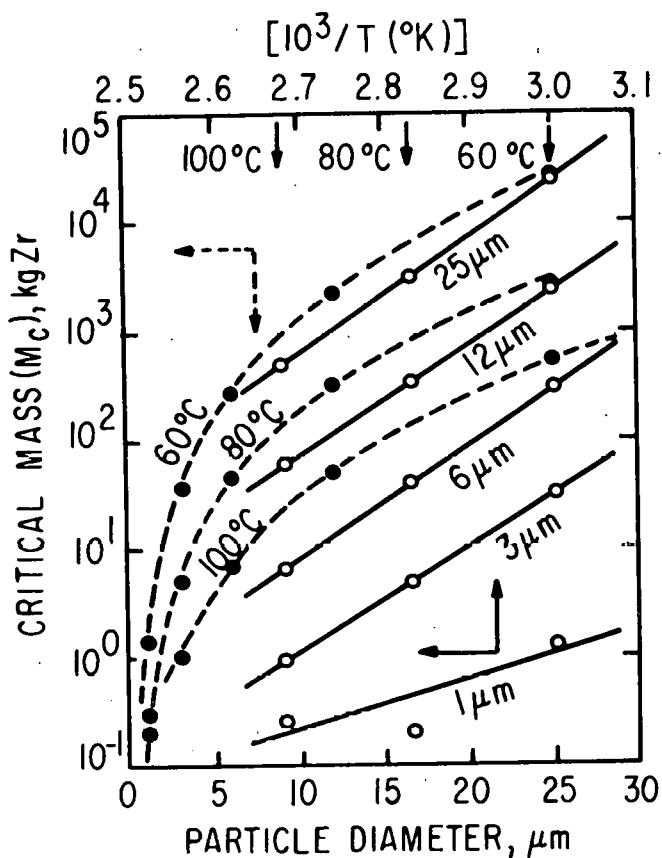


Fig. 1.  
Relation of Ignition Critical Mass  
to Size of Spherical Particles of  
Zirconium (adapted from DeHollander)

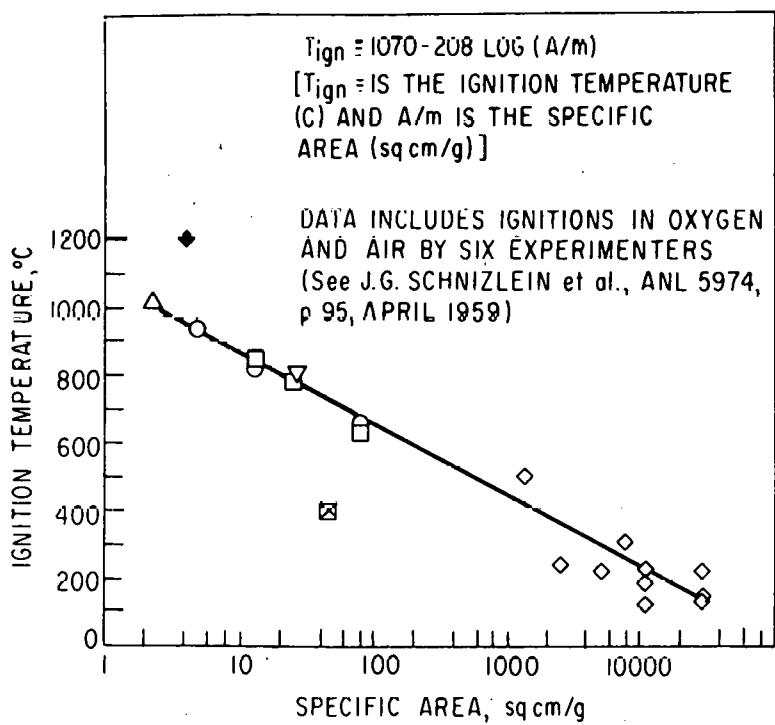


Fig. 2. Ignition Temperature of Zirconium Foils as a Function of Specific Area [Schnizlein].

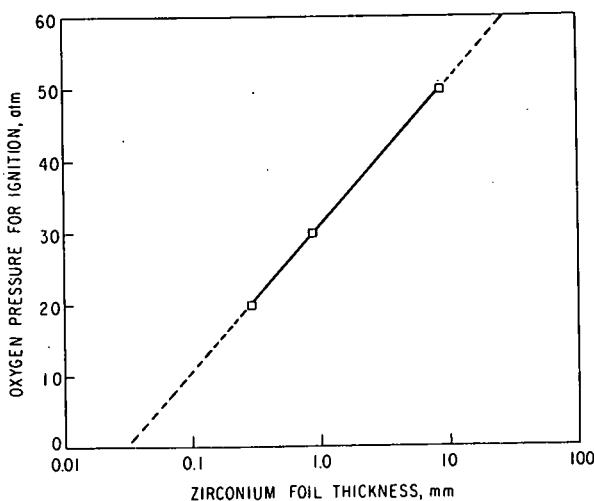


Fig. 3. Plot of the Relationship between Zirconium Foil Thickness and Oxygen Pressure for Ignition at 25°C [Littman].

Table 5. Relationship Between Thickness of Zirconium Foil and Minimum Oxygen Pressure for Ignition at 25°C [Littman].

Foil Thickness		Surface to Volume Ratio		Specific Area,	Oxygen Pressure for Ignition,
mm	in.	$\text{cm}^{-1}$	$\text{in.}^{-1}$	$\text{cm}^2/\text{g}$	atm
0.3	0.01	80	200	12.5	20
0.9	0.035	24	60	4.0	30
9.0	0.350	4.1	15	1.7	50

gradually evolved [Allison, Bulmer]. Recommendations for handling zirconium and its alloys, not aimed specifically at hulls or the accompanying fines, are summarized in Table 6. These data are to be related to the management of hulls by use of a reference case discussed in Section V.

### III. RECAPITULATION OF RESEARCH RESULTS

An orderly analysis of the available information was obtained by categorizing the large and diverse body of data according to topics found to be important to zirconium pyrophoricity. The categories wherein the literature yielded results are:

- (1) Effects of water, moisture, and humidity,
- (2) Effects of particle size,
- (3) Effects of surface area,

Table 6. Some Recommendations for Safe Handling of Zirconium and Its Alloys [Allison, Bulmer].

- 
- Eliminate other combustible materials (limit source or spread of fire).
  - Maintain moisture content below 3% or completely submerge in water.
  - Avoid use of water or CO<sub>2</sub> extinguishers in the event of a fire. It is preferable to let burning zirconium expire of its own accord. In some cases, dry inert powder extinguishers may be used; descending orders of effectiveness are shown by ternary chloride eutectic, sodium chloride base powders (proprietary), zirconium silicate, sand, kieselguhr (hydrated forms of silica, diatoms), graphite, dolomite (limestone).
  - Use water-soluble oils in machining.
  - Avoid, in particular, accumulations of fine material, *e.g.*, dust accumulations should be less than 20 g/m<sup>2</sup> (0.007 oz/ft<sup>2</sup>).
  - Avoid sources of ignition.
  - Avoid above-ambient (or extreme) temperature.
  - Use diluent, such as sand, at least 1:1 by volume.
  - Metal considered a hazard from a particle size standpoint should be oxidized (converted to a stable form).
  - Consider use of inert gas such as argon in special situations.
  - Avoid mixing of zirconium with other metals (materials).
  - Provide for venting of hydrogen.
  - Separate storage area from other work areas.
  - Compact scrap to enhance safety.
  - Limit quantities to be disposed of by burning to <34 kg; use thin (15-25 cm) layers instead of deep-bed configurations.
  - Avoid fuse conditions--whereby a small amount of fine material ignites coarser material.
  - Exercise care in transferring scrap.
- 

- (4) Effects due to the condition of the surface,
- (5) Effects due to the composition,
- (6) Effects of mechanical forces,
- (7) Effects of electrostatic energy.

A detailed outline of the categories is presented in Appendix A. A summary of the results is given in the following section. It should be noted that almost all of the data obtained to date are based on the use of unirradiated zirconium or Zircaloy. Although there are adequate reasons to assume no significant practical differences in the pyrophoric behavior of irradiated (and leached) Zircaloy and unirradiated Zircaloy, the absence of direct experimental verification of this similarity suggests that a conservative approach to the pyrophoricity of cladding hulls is desirable.

A. Research\*1. Water, Moisture, and Humidity Effects (I.A.1, 2, 3, and 4)

Data on the effects of water, moisture, and humidity on the oxidation and combustion of zirconium and Zircaloy are quite extensive. Many of the data are related to the use of Zircaloy in LWR environments. In the temperature range 200-350°C, it was found that water vapor reacts with zirconium at the same rate as elemental oxygen. Above 350°C, hydrogen gas is liberated, suggesting a decomposition of the zirconium hydride.

The burning of zirconium wire immersed in water was reduced or eliminated by increasing the water temperature. It was also found that the larger the diameter of wire, the more difficult it was to extinguish burning with water. With regard to water, recommendations for handling zirconium powders warn that a dangerous condition could exist with a moisture content between 3 and 25 wt %. It is also suggested that powders completely submerged in water are in a "safe" condition. There has been some experience, however, of detonations of zirconium powders submerged in water. One source investigated the ignition of zirconium in air and found that the humidity of the air was not an important factor in zirconium ignition [I00-1956].

2. Particle-Size Effects (I.C.1)

Tests with particle size as a variant are also reported exhaustively. It was shown that particles with average diameters of 3  $\mu\text{m}$  or less ignited spontaneously when released as a cloud, in air, at room temperature. Particles with average diameters of about 18  $\mu\text{m}$ , on the other hand, had to be heated to 350°C to ignite under otherwise identical conditions. A layer of 3- $\mu\text{m}$  zirconium powder ignited at 190°C in air, at 620°C in carbon dioxide, and at 790°C in nitrogen.

An attempt to categorize the particle-size effect on pyrophoricity resulted in the following ranges: (1) material consisting of zirconium particles of 60- $\mu\text{m}$  dia or less is likely to be explosive, and (2) zirconium material of particle size 60- to 850- $\mu\text{m}$  dia is likely to be a hazardous fire risk. Industrial experience (from Table 3) indicates that 90% of the fines produced during chopping of unirradiated, nuclear-grade Zircaloy tubing have diameters larger than 700  $\mu\text{m}$ .

3. Surface-Area Effects (I.C.2)

A correlation is available (see Fig. 2) that describes the relation between surface area and the ignition temperature of zirconium. It is expressed

$$T_{\text{ign}} (\text{°C}) = 1070 - 208 \log S$$

where  $S$  is the specific area in  $\text{cm}^2/\text{g}$ . This expression was derived from tests using zirconium foils of various thicknesses in oxygen or air at

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\* Omitted references can be found in Appendix A. The section numbers in parentheses pertain to relevant categories in Appendix A.

atmospheric pressure. The foils were heated by electrical resistance to ignition temperatures. Other data were obtained relating zirconium foil thickness to the minimum oxygen pressures required to cause ignition at room temperature. The results were presented previously in Fig. 3 and Table 5 and are correlated by the expression,

$$P_{\text{atm}} = 18.7 \log T_{\text{cm}} + 50$$

where  $P_{\text{atm}}$  is the oxygen pressure in atmospheres and  $T_{\text{cm}}$  is sample thickness in cm.

Material with a specific area of about  $9200 \text{ cm}^2/\text{g}$  (typified by  $1\text{-}\mu\text{m}$ -sized spherical powders) and a surface-to-volume (S/V) ratio of 60,000 is considered pyrophoric, while material one-tenth the specific area and S/V ratio is deemed to be borderline between hazardous and safe. For zirconium sheet, material with a specific area below  $12.7 \text{ cm}^2/\text{g}$  and a S/V ratio below 82.7 (corresponds to 0.025-cm-thick material) is considered stable under normal handling conditions.

#### 4. Surface-Condition Effects (I.C.3)

Roughening of the surface of any given form of zirconium has the effect of lowering the temperature required for ignition, *i.e.*, increasing the pyrophoricity. Other research, however, indicates that surface treatment (mechanical or chemical polishing, abrasion, etc.) has little effect on oxidation of zirconium specimens. Results of another program showed that a wide extent of surface oxidation of zirconium resulted in little or no difference in ignition potential. The same was true for surface-hydrided material. Zirconium that was surface-carbided, however, was considerably less susceptible to ignition than "clean," oxidized, or hydrided metal.

In other work in which the pressure of pure oxygen at room temperature was investigated as a variable in the ignition of zirconium and Zircaloy foils, it was found that metal with a mechanically cleaned surface (oxide-free), metal that had been etched with a  $\text{HNO}_3 - \text{HF}$  solution, and metal that had been surface-hydrided (from 4 to 30% hydride) all ignited at oxygen pressures of 300 psi and above. Zirconium foils with an oxide film ignited at a minimum of 400-psi oxygen. Zircaloy-2 samples etched in the same manner as the zirconium resisted ignition to an oxygen pressure of 450 psi. Zirconium foil samples, surface-carbided to 10% carbide, resisted ignition up to oxygen pressures of 1500 psi.

#### 5. Material-Composition Effects (I.C.4)

In an investigation of oxidation rates of binary alloys of zirconium, the following effects were observed. Alloys with copper, nickel, beryllium, or hafnium reduced the oxidation rates as compared to pure zirconium. Metals whose binary alloys with zirconium showed an increased oxidation rate were chromium, cobalt, platinum, iron, tungsten, uranium, molybdenum, lead, niobium, tantalum, vanadium, titanium, aluminum, silicon, and tin. The study also showed that increasing the carbon content of pure zirconium also increased the oxidation rate.

Results of another effort showed that an increase of hydrogen in solid solution increased the pyrophoricity of crystal-bar zirconium wire. As seen in Fig. 4, a hydrogen increase from 1 to  $\sim$ 150 ppm decreased the required ignition energy by  $\sim$ 40 cal/g (167 J/g); a further hydrogen increase of two orders of magnitude (to 16,000 ppm H) decreased the required ignition energy by only  $\sim$ 5 cal/g (21 J/g). Conversely, increasing the oxygen content in zirconium wire to correspond to a  $\sim$ 3% weight gain ( $\sim$ 30,000 ppm oxygen) resulted in an increase of the required ignition energy of  $\sim$ 50 cal/g (209 J/g).

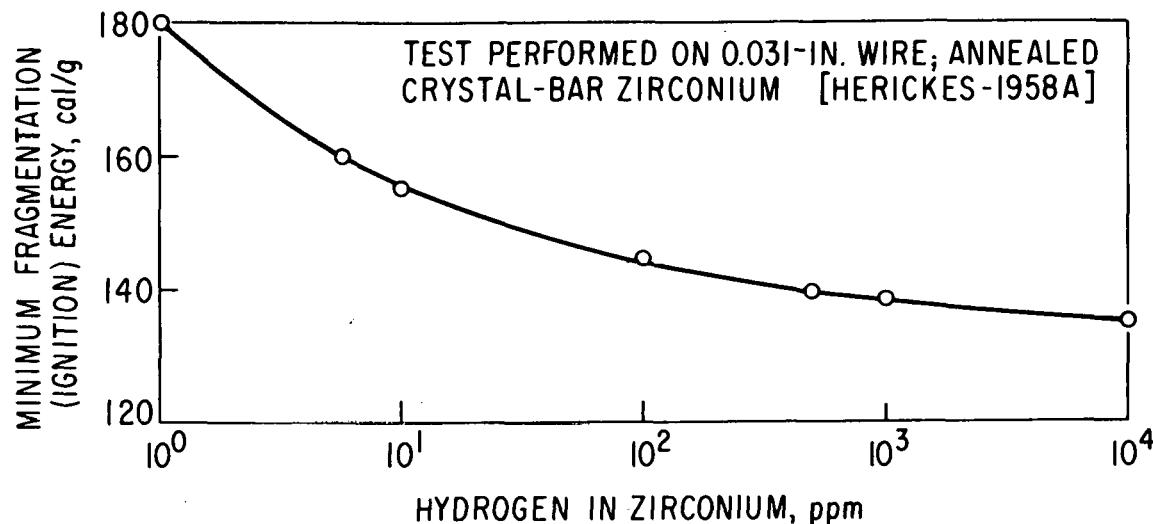


Fig. 4. The Effects of Hydride Content on the Ignition Energies for Zirconium Wire

#### 6. Mechanical-Force Effects (II.A.1 and 2)

Zirconium, Zr-2\* and Zr-3\* scrap of various forms (0.03- to 0.8-mm thick  $\times$  0.1- to 19-mm wide) were subjected to modest impact and friction tests. The samples, in the dry condition in air, did not ignite on impacts up to 73 J. Friction tests with the same material, using a 20-kg pendulum released 1.5 m above sample level, resulted in no ignition. Each of the thirteen samples was struck the same number of times while being observed for the production of sparks. Results were given as the percentage of pendulum strikes that produced sparks. From 1 to 32% sparking was reported for each sample in the dry condition; 0 to 10% sparking while in the wet condition.

\*Zr-2 (Zircaloy 2) is a zirconium alloy containing 1.5% Sn, 0.12% Fe, 0.1% Cr, and 0.05% Ni.

Zr-3 (Zircaloy 3) is a zirconium alloy containing 0.3% Sn and 0.3% Fe.

In another investigation, zirconium strip immersed in liquid oxygen ignited at threshold impacts of 170 J. The same form of zirconium in pure gaseous oxygen resisted ignition from impacts to the 170-J test limit.

#### 7. Electrostatic-Energy Effects (II.B.2)

Tests with zirconium powders showed that cloud dispersions of 3- $\mu\text{m}$  particles at threshold concentrations of 0.045 g/L of air (often resulting in spontaneous combustion) required electrostatic discharges of 15 mJ for ignition, while layers of the same-sized particles ignited with only a 0.0064-mJ discharge. Dust clouds of 18- $\mu\text{m}$  particles ignited at 12-mJ discharges and with only 0.24-mJ discharges when in the dust layer mode.

Although no data were found on the effect of static electrical discharge on larger zirconium forms, it should be noted that in tests to determine surface-area effects (described previously), zirconium foils were subjected to conduction of high-voltage discharges in order to establish ignition temperatures as induced by resistance heating.

#### B. Interpretation of Results

Results of tests on zirconium and, less extensively, Zircaloys point to the conclusion that a pyrophoric hazard may exist only when the material is subdivided into small particles. In this regard, zirconium and Zircaloys appear to present problems comparable to those associated with the handling of many other commercial materials. Massive zirconium (*i.e.*, objects whose smallest dimension is greater than 0.3 mm) exhibits capabilities for surface reaction with the major constituents of air (nitrogen, oxygen, and carbon dioxide) at elevated temperature. While the reported results do not prove that Zircaloy, in the form of fuel cladding tube, is *not* a pyrophoric hazard, they do not suggest, on the other hand, that Zircaloy, in that form, *is* pyrophoric under hull handling and storage conditions.

Conversely, tests and experience have shown zirconium fines to be a definite pyrophoric hazard. No adequate data exist showing that zirconium fines mixed with hulls are less pyrophoric than fines alone. Further, no direct information has been developed that identifies any modification of pyrophoricity by irradiation and acid leaching. No incidence of pyrophoric behavior has been reported in any work dealing with irradiated cladding from LWR oxidic fuel. Further, in the actual handling and burial-storage of waste zirconium hulls from LWR fuels at a fuel reprocessing plant, no problems have been reported involving potential ignition hazards.

The lack of pyrophoricity data on irradiated, leached Zircaloy hulls necessitates extrapolation of information obtained with unirradiated materials. This extrapolation appears to be of relatively low risk, allowing recommended procedures to be applied to the Zircaloy waste stream with adequate confidence.

#### IV. RECENT INVESTIGATIONS RELATED TO THE PYROPHORICITY OF ZIRCALOY

More recently, the ignition behavior of Zircaloy was investigated in tests performed on various forms of metal, such as fines from a dry tube-chopping operation, saw fines in which a water-soluble oil was used as coolant, and single tubing segments. Tests were both qualitative and quantitative. Results of these tests and other related work are summarized in this section.

A. Summary of Ignition Test Work

1. Tests on Tubing Segments

Oxidation tests on single sections of unirradiated Zircaloy tubing at 700, 800, and 900°C for 1-hr periods show that average oxidation rates essentially tripled with each 100°C increase in temperature; however, the extent of oxidation was only 13% for the test at the highest temperature. No signs of ignition were evident [Steindler].

A series of ignition tests with single, 8-mm-long sections of unirradiated Zircaloy-4 tubing were made at TWCA\*, using zirconium igniter powders. The test data (see Table 7) show that tubing with an 0.8-mm wall did not ignite even with an 8:1 weight ratio of igniter powder to tubing, although surface oxidation was noted in each case. Temperatures of 1600°C were reached in some tests. Self-heating of Zircaloy, indicative of sustained reaction, has been observed in tests involving the reaction of Zircaloy with steam at temperatures in the region of the melting point (~1850°C) [Ivins].

These data are in agreement with the conclusions from the literature survey that Zircaloy tubing does not represent a pyrophoricity hazard.

2. Behavior of Zinc-Coated Material

Coating of Zircaloy hulls with zinc was considered a process option to mitigate the pyrophoric hazard. Simple ignition tests were performed to observe the behavior of zinc-coated tubing. Coating was achieved by dipping the sample in a zinc bath for 10-15 min at 575°C. After cooling, a gas-oxygen torch flame (1400°C) was applied to the sample. The result was oxidation of the coated tubing, similar to that experienced with unoxidized material, but no ignition occurred. A less intensive heat source, *i.e.*, a match flame (estimated temperature 500°C), had no effect on the coating [Steindler].

Ignition tests with zinc-coated Zircaloy saw fines and turnings, using a gas-oxygen torch, resulted in spalling of the zinc, probably as the oxide, and ignition of the Zircaloy. A match flame had no visible effect. Thus, zinc coating of hulls does not appear to alter the ignition properties of Zircaloy materials and does not appear to reduce the pyrophoricity of fines, which is noted below.

3. Miscellaneous Ignitions Tests

Exploratory ignition tests on several Zircaloy forms having relatively high surface-to-volume ratios gave the following results: (1) dry, clean turnings could not be ignited with a match, but did ignite with a gas-oxygen torch, as in the test with zinc-coated material, (2) a small pellet made of saw fines could not be ignited with sparks or a match, but did ignite and burn quickly when heated with a gas-oxygen torch; compaction

\* Teledyne Wah Chang Albany Co., Albany, Oregon

Table 7. Ignition Tests Performed on Zircaloy Tubing Sections

Tubing section dimensions: 8-mm length x 15-mm dia x 0.8-mm wall for all tests except tests 5 and 6 which used a half-ring section; corresponding weights were 1.5 and 0.75 g, respectively.

Ignition powders: -300 mesh ( $\sim 50 \mu\text{m}$ ) Zircaloy-2 powder prepared by a hydriding-dehydriding step for tests 1-5; 18-20  $\mu\text{m}$  zirconium sponge powder (leached for removal of residual  $\text{MgCl}_2$ ) for tests 6-9.

Tubing material: Clean Zr-4 for all tests except test 7 which used an autoclaved, hydrided section containing 100 ppm hydrogen.

Heat source: Gas torch; in addition, an oxygen torch was used in test 9.

Initial Conditions: Materials at ambient conditions on a ceramic base.

Test No.	Powder Mass, g	Powder-to-Test Piece Weight Ratio	Powder Ignition Temp, °C	Powder Burn Time, s	Maximum Attained, °C	Remarks
1	0.375	0.25	430	30	822	
2	1.5	1	430	80	585	
3	3.0	2	430	50	941	
4	6.0	4	430	70	894	
5	6.0	8	430	25	1150	Tubing did not ignite; all tubes had an oxidized surface after the test.
6	6.0	8	400	60	798	
7	6.0	4	400	50	1098	
8	6.0	4	400	65	1600	Burning powder plus torch used in attempt to ignite tubing section.
9	6.0	4	400	70	1600	Tubing only glowed, and only as long as torch was applied.

often reduces the tendency to ignite, but this is a function of particle size, mass, etc., (3) uncompacted saw fines could not be ignited with sparks from a torch lighter but did ignite with a match [Steindler].

Other tests involved water and 1-in.-long tubing sections. The tubes were quickly heated in air to 800°C and (1) sprayed with atomized water or (2) immersed into a beaker of water. No signs of ignition were noted, although the heating resulted in the development of an oxide coating.

#### 4. Hardness Measurements on Zircaloy

No correlation between hardness and pyrophoric behavior of Zircaloy has been found in the literature, but hardness is considered pertinent to an overall characterization of zirconium materials. Hardness measurements were made on several Zircaloy materials [Steindler]. Materials included stock Zircaloy tubing, hydrided tubing with hydrogen contents of 100, 250, and 300 ppm, tubing oxidized in air at 350°C for two hours, and autoclaved tubing. The test results are shown in Table 8. A value for irradiated Zircaloy-2 is included for comparison [Megerth].

Table 8. Superficial Hardness of Zircaloy-2 Tubing

	Rockwell C Hardness Number
Untreated-hydrogen, 25 ppm <sup>a</sup>	62
Hydrided-hydrogen, 100 ppm <sup>a</sup>	60
Hydrided-hydrogen, 250 ppm <sup>a</sup>	60.7
Hydrided-hydrogen, 300 ppm <sup>a</sup>	60.4
Air-Oxidized <sup>a</sup>	57.5
Nonautoclaved <sup>b</sup>	63.2
Autoclaved <sup>b</sup>	63.8
Experimental-preirradiation <sup>c</sup>	58.8
Experimental-irradiated <sup>c</sup>	63.8

<sup>a</sup>Stock tubing, 1.3-cm OD x 2.5-cm long x 0.8-mm wall thickness [Steindler].

<sup>b</sup>Commercial reactor tubing [Steindler].

<sup>c</sup>Tubing used in irradiation experiments [Megerth].

Similar Rockwell hardness values were obtained for the three hydrided materials, while the stock tubing (unexpectedly) appeared to be somewhat harder. One possible explanation is that the hydrided tubing underwent annealing at the hydriding temperature, 600°C. Autoclaving appears to put a hard finish on the tubing as indicated by the values obtained. The value for irradiated material was similar to that for the autoclaved sample. The air-oxidized tube gave the lowest value, possibly because annealing occurred while it was heated.

A related concern is embrittlement of Zircaloy, which occurs with irradiation and increasing hydrogen content. Hardness is assumed to be characteristic of embrittlement, but no relationship between embrittlement and pyrophoricity has been reported. However, if such a relationship should exist, annealing of the Zircaloy hulls may represent a means of desensitizing the material.

#### B. Observations of the Handling of Scrap Zircaloy

The Teledyne Wah Chang Albany Co. is a major U.S. producer of raw and wrought zirconium and nuclear grade Zircaloy tube blanks. Observations were made of how the company handles a variety of scrap Zircaloy forms, including unirradiated fuel clad tubing that had been returned for possible recycle. Various mechanical processes were observed in operation and they are described in detail below.

##### 1. Dry-Chopping of Scrap Zircaloy

Various amounts of off-specification Zircaloy tubing are returned from tubing manufacturers to TWCA for recycle. Rework includes cleaning, chopping, compaction, welding of compacts into electrodes, and arc-melting. Dry, clean tubing is fed to a chopper that produces segments several centimeters in length; no coolant is employed. A relatively small amount of fines is produced and collected in 200 liter drums, along with the tubing sections, for transfer to the compaction area or to interim storage. The fines fraction is estimated at <0.01. A nominal size distribution for this material was shown in Table 3. In the experience of the operator, these fines do not represent a pyrophoric hazard, although individual particles may burn. It was suggested that even complete combustion of the dispersed fines in a drum would be insufficient to cause ignition of the contained tubing segments.

##### 2. Hammer Milling of Scrap Zircaloy

Hammer milling of scrap Zircaloy, such as turnings from lathe operations, is done at TWCA to facilitate subsequent operations such as compaction and to increase the loading of drums for interim storage. The routine milling operation is characterized by rather intense sparking, but the trays that receive the milled scrap are sprayed continuously and rather heavily with water. Ignition is rare although not completely eliminated by use of water. Consequences of ignition are minimized by avoiding the accumulation of fine material.

### 3. Sawing of Zircaloy Ingots

Wet-sawing of massive Zircaloy ingots is done on conventional equipment, using a water-soluble coolant. The saw fines tend largely to be spiral rather than sphere-like particles and as with other fine materials, good housekeeping is a prime requisite to safety. The fine cuttings are generally stored under water in 200-liter drums until recycled. These are often too highly contaminated with oxygen and nitrogen for direct recycle to the nuclear-grade metal line but can be used in steel making and in the production of "lower-grade" zirconium items.

### 4. Washing of Scrap

Various scrap material having relatively small dimensions, such as lathe turnings, is washed routinely with detergent in a large revolving machine of the cement-mixer type. Scrap is moved into and out of the bowl of the washer by an auger. Because of the large batch size, about two tons, attention to safety is particularly important. Safety provisions include water flooding of the scrap and minimizing spark sources by, for example, the use of wooden push rods. To avoid large accumulations of fine material, the large washed batches are divided into much smaller batches before drying with warm air. The drying operation transfers the scrap through the apparently critical moisture region (15% water), but relatively little difficulty from ignition has arisen from clean scrap. Fires, once started, are allowed to burn out and no attempt is made to extinguish them.

### 5. Compaction Tests

Mechanical compaction of Zircaloy hulls has been suggested as a process option in hulls management because of the volume reduction factor and improved heat transfer characteristics of the compacts. Mechanical compaction of chopped, off-specification tubing is a commercial scrap handling operation at TWCA [Tetz]. Operation of a large, hydraulic press produced 36-kg compacts (see Fig. 5), about 28 cm in diameter by 13 cm high when compacted to about 72% of theoretical density. A pressure of  $3.6 \times 10^8$  Pa (52,000 psi) was used.

This press also handled relatively heavy sections (e.g., tube blank sections with a 3-mm wall thickness) in the course of compacting ordinary (~0.9-mm wall) tubing and fines that come from a tube chopping operation. The fines represented a rather small fraction of the charge and appeared to pose no pyrophoricity hazard in the operation. Material that accumulated around the die cavity was blown away (dispersed) with an air jet. Machine turnings and saw fines have also been handled routinely in the press.

### C. Application of Recent Results

Results of some recent studies [Steindler] can be summarized and related to LWR hulls as follows:

1. Zircaloy materials of relatively high surface area, such as saw fines and turnings, exhibit pyrophoric behavior. This agrees with literature results and experience of others; these data are believed applicable to fines in hull waste.



Fig. 5. Zircaloy Tubing Compacts Prepared by Mechanical Compaction  
(courtesy Teledyne Wah Chang Albany Co., Albany, Oregon)

2. Compacted fines can be ignited with relatively moderate heat sources, *e.g.*, a gas-oxygen torch and, after ignition, can reach high temperatures; fines, therefore, can serve as a source of ignition for materials other than hulls.
3. Single tubing segments similar in size and shape to hulls do not ignite when in contact with burning Zircaloy fines at temperatures to about 1600°C. Preliminary data from high-energy shock-ignition tests\* on compacted and noncompacted unirradiated Zircaloy tubing segments (600 and ~2500 g samples) indicate that ignition can occur if the melting point (1850°C) is exceeded, but that burning is not sustained. Large scale tests on tubing segments need to be done to verify that pyrophoric behavior is not a "critical mass" function.
4. Commercial quantities of fine zirconium materials are handled routinely in scrap milling, compaction, and other operations, under totally dry or totally submerged conditions. Somewhat smaller quantities (half-full 100- to 200-liter drums) of scrap with intermediate amounts of moisture are being handled. The safe handling of Zircaloy fines rests largely on continued surveillance to ensure a controlled environment.

\*Performed by Shock Hydrodynamics, Inc., North Hollywood, California.

## V. A MODEL FOR HULLS PRODUCTION AND MANAGEMENT AS A REFERENCE CASE

A. A Description of the Model

The generation and handling of the Zircaloy cladding waste stream is described below in a model head-end flow sheet and hulls management procedure to aid in the evaluation of the importance of pyrophoric behavior. The model is intended to represent a low risk approach. It includes process steps that evolved from the review of information on zirconium pyrophoricity and on current and proposed reprocessing ideas. The model includes the concept of a Federal repository remote from the reprocessing site. The general configuration of the Barnwell Plant chop-leach head-end flowsheet, as described in the safety analysis report [AGNS], has been adopted for this model. Modifications [Schofield] introduced subsequent to the finalization of the safety report are included in some instances.

The reference flowsheet is shown in Fig. 6. Intact fuel assemblies are chopped to produce 5- to 13-cm-long pieces of fuel elements that drop into a basket located in the dissolver. Cocurrent air and water is used to flush the shear and fuel chute and to transport small particles into the basket. Since no separate handling is provided for metallic parts of the fuel assembly that do not contain fuel, the mixture in the basket consists of Zircaloy-clad fuel pieces, Zircaloy fines, Inconel or Zircaloy sheet-metal grid sections and springs, and stainless steel end fittings.

The fuel is dissolved and leached from the cladding by nitric acid. The Zircaloy cladding and fuel assembly hardware are essentially unattacked by the acid. Circulation of nitric acid through the basket transports some amount of the metal fines, as well as undissolved fuel fines, from the basket into the dissolver barrel. Removal of the basket, containing the bulk of the undissolved metallic components, is preceded by rinsing the hulls with dilute acid to ensure a high degree of fuel removal. After removal, the contents of the basket are monitored for excessive undissolved fuel. If the activity is satisfactorily low, the metal waste is dumped into a storage container. During this operation, the Barnwell design provides a sand-dump capability that is activated if Zircaloy ignition should occur. It is expected that a large percentage of the Zircaloy fines will remain as a heel in the dissolvers, to be periodically removed and combined with the sludge from the feed-clarification centrifuges. In the reference flowsheet, the combined fines would then be oxidized and returned to the hulls stream for packaging.

The hulls storage container is a heavy-wall stainless steel cylinder, approximately 1.07-m ID by 2.29 m high. The containers, after being sealed with a tight cover and gasket, could serve as the primary containers when hulls are shipped to a Federal repository. Each container is expected to hold approximately 1.6 tonne\* of metallic waste generated by the treatment of about 5 tonnes of spent fuel.

The hull wastes, including assembly hardware, have the composition shown in Table 9. A previous table (Table 3) indicates the size distribution of the fines before oxidation. Analytical and computational results for the

\* One tonne = one metric ton = 1000 kg.

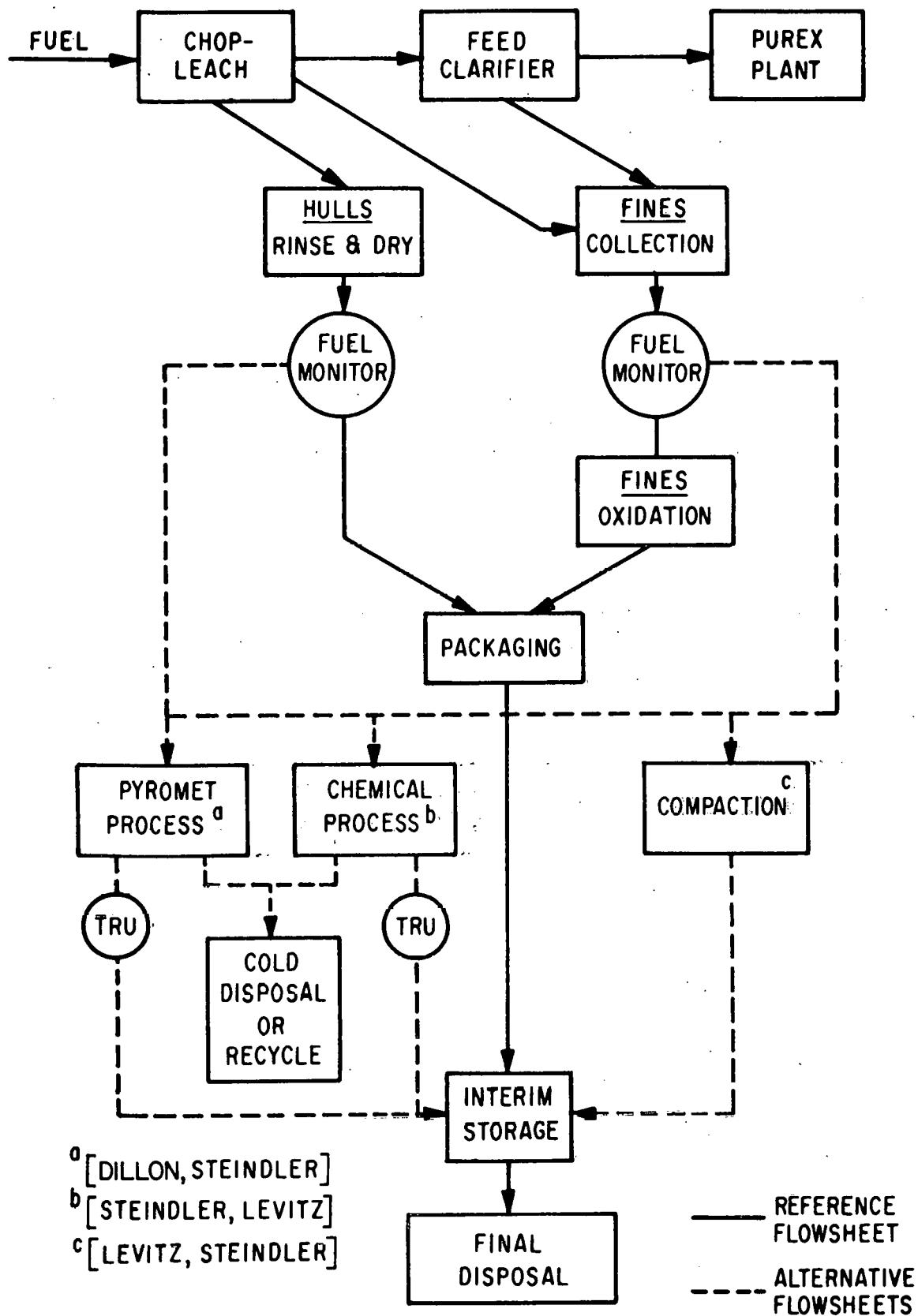


Fig. 6. Reference Hulls Management Flowsheet

Table 9. Comparison of Component Proportions in Waste LWR Fuel Cladding Mixtures

	PWR <sup>a</sup>		BWR <sup>a</sup>		Reference MOX <sup>b</sup>	
	kg/MTHM <sup>c</sup>	wt %	kg/MTHM	wt %	kg/MTHM	wt %
Zircaloy Hulls	226.8	70.6	262.7	78.4	287.3	88.4
Zircaloy Fines <sup>d</sup>	0.23	0.07	0.26	0.08	0.29	0.09
Stainless Steel	66	20.6	44	13.1	28.9	8.89
Inconel	27	8.4	27	8.06	8.03	2.47
Residual Fuel	1 <sup>e</sup>	0.31	1 <sup>e</sup>	0.30	0.5 <sup>f</sup>	0.15
Total	321	100	335	100	325	100

<sup>a</sup>[Griggs].<sup>b</sup>[ERDA].<sup>c</sup>MTHM = metric ton of heavy metal in spent fuel.<sup>d</sup>Based on 0.1 wt % of total Zircaloy.<sup>e</sup>Based on 0.1 wt % of one MT(U+Pu)<sup>f</sup>Based on 0.05 wt % of one MT(U+Pu).

transuranic composition of the hull waste are given in Table 10. The distribution of radioactive elements from fissioned fuel and from activation products is listed in Appendix B. Table 11 shows the heat generation rate of the hulls, and Fig. 7 shows the effect of cooling time (radioactive decay). Hulls from 1 tonne of spent fuel are expected to generate about 1 kW at 160 days after removal of the assemblies from the reactor. It is likely that this heat is more than adequate to remove residual moisture from hulls, so on-site storage is considered to be dry.

Sludge from the feed clarification step and the contained Zircaloy fines in the sludge represent a special problem. The model flowsheet (Fig. 6) shows that this material is oxidized to deactivate the Zircaloy fines and that the oxidized material is discarded with the hulls. If the sludge contains a significant quantity of undissolved fuel, it may be subjected to additional leaching.

Hulls and other hardware, including the coarser fines produced during chopping, are stored in the receivers at the reprocessing plant for an interim period. Above-ground storage in secondary containers that provide adequate shielding is contemplated for the AGNS plant and, if used, would not affect the hulls since the containers are to have sufficient integrity to maintain the original environment for at least the time estimated for on-site storage (before off-site shipment). Included in this criterion is the absence of deleterious reaction between the container and the waste metals.

The model head-end flowsheet and hulls management procedure includes handling of this waste after the interim on-site storage time has elapsed (minimum of 90 days after reactor discharge). However, no design criteria or regulations exist as guidance for the subsequent steps. Since hulls represent a special category of waste, *i.e.*, they are a transuranic (TRU)

Table 10. Analyzed and Calculated Concentrations of Transuranic Nuclides in Spent Fuel Cladding Hulls (nCi/g)

Nuclide	No burnup data given [Griggs 1975, 1975A]	ANALYSIS		CALCULATED	
		0.1% fuel contam., 250 kg Zr/MTHM			
		35,000 MWd/MTHM 40 MW/MTHM	34,000 MWd/MTHM 29.5 MW/MTHM	[AGNS]	[Haug]
Neptunium-237	--	--	--	0.4	
Neptunium-238	--	0.02	--		
Neptunium-239	--	--	20		
Plutonium-236	--	--	0.3		
Plutonium-238	2.6	10	10		
Plutonium-239	0.49	1	1		
Plutonium-240	0.70	2	2		
Plutonium-241	256	640	420		
Plutonium-242	0.007	--	--		
Americium-241	1.11	1	0.6		
Americium-242 <sub>m</sub>	--	--	0.04		
Americium-242	--	0.02	0.04		
Americium-243	0.08	--	0.08		
Curium-242	9.5	160	80		
Curium-243	--	0.08	0.01		
Curium-244	9.8	10	10		
Curium-245	--	--	0.4		

waste and also have a high beta-gamma component but do not fall under the definition of a high level waste, shipment of the hulls to a retrievable storage waste repository is contemplated, as required for TRU wastes. It is assumed that repackaging of the hulls at the reprocessing plant\* will not be required. Shipment of hulls is expected to be by large rail cask of the type used for spent fuel shipments. Handling at the repository may include repackaging, decontamination to remove actinides, salvage of metals, or consolidation of metals into high-density forms. These operations are expected to be carried out under conditions where pyrophoric behavior at a modest scale would not be disruptive or excessively hazardous.

Also shown in Fig. 6 are alternatives for handling of hull waste. The use of a compaction step [Levitz] would result in a reduction of the volume of metal waste destined for storage. Both the pyrometallurgical [Dillon] and chemical [Steindler] processes indicate a possible separation of the waste stream into a large-volume, low-activity, easily-disposed-of fraction essentially free of TRU elements, and a low-volume, high-activity fraction to be stored in its final form or possibly added to the high-level waste before that stream is processed for storage. A chemical process (ZrCl<sub>4</sub> volatilization) is currently under investigation at Argonne (see Appen. C).

\* If such repackaging is required, design of the primary container to allow monitoring and control of the atmosphere in the container appears prudent.

Table 11. Calculated Heat Generation in Zircaloy Cladding Hulls

Source	Thermal Power in watts/kg of Cladding			
	[Schofield]	[AGNS]	[ORNL-4451]	[Haug]
	35,000 MWd/MTU 4C MW/MTU 190-d cool	35,000 MWd/MTU 40 MW/MTU 160-d cool	33,000 MWd/MTU 30 MW/MTU 150-d cool	34,000 MWd/MTU 29.5 MW/MTU 150-d cool
alpha	0.177	0.0065	--	--
beta		0.039	--	--
gamma	0.903	0.028	--	--
fission prod.	--	--	0.077	0.054
actinide	--	--	0.003	0.003
activation prod.	--	--	0.827	0.378
total power, W/kg clad	1.08 <sup>a</sup>	0.074 <sup>b</sup>	0.907 <sup>c</sup>	0.435 <sup>c</sup>

<sup>a</sup>Fuel contamination of 0.5% plus induced activity in Zircaloy.

<sup>b</sup>Calculated 0.1% fuel contamination only.

<sup>c</sup>Calculated 0.1% fuel contamination plus induced activity in Zircaloy.

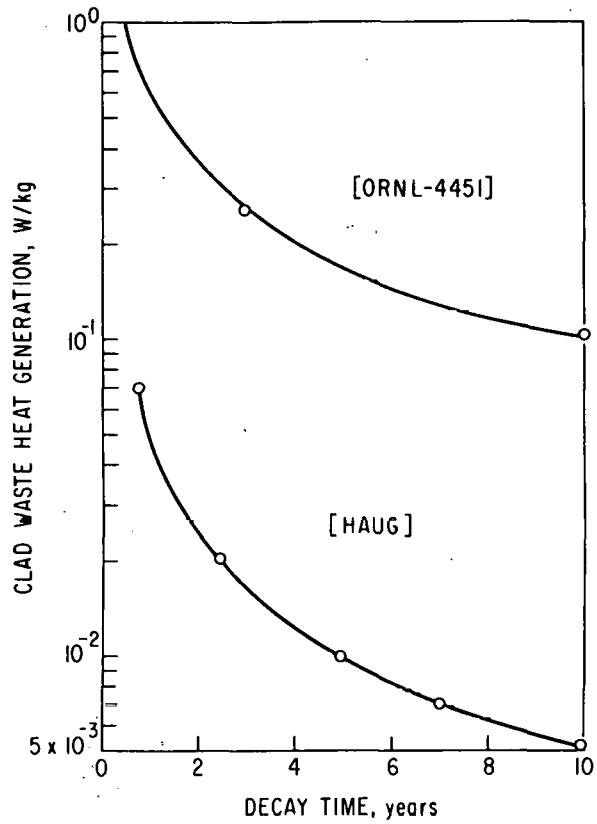


Fig. 7. Two Estimates of Zircaloy Cladding Heat Generation Decay

and pyrometallurgical methods (principally smelting) are being studied at Battelle's Pacific Northwest Laboratories [Dillon]. These and other options have been summarized in a recent review of technology alternatives [ERDA].

#### B. Discussion of the Model in Regard to the Pyrophoricity Question

From the outset, it should be stated that the model represents a compromise in terms of selection of an overall flowsheet since designs for three other reprocessing plants exist,\* in addition to the AGNS plant. Some of the process steps employed in these other plants represent options pertinent to the pyrophoricity question. The present model aims mainly to reduce the risk of pyrophoric behavior and any attendant release of radioactivity to the biosphere. The model also reflects the assessment of the state of knowledge regarding the potential for pyrophoric behavior in the Zircaloy hulls waste streams.

\*The General Electric Midwest Fuel Reprocessing Plant (MFRP) at Morris, Illinois terminated operations in 1974 after a period of cold testing [DOCK 50-268]. The Nuclear Fuel Services (NFS) plant is at West Valley, New York [DOCK 50-201]. Exxon Nuclear Company has recently submitted plans to build a plant in eastern Tennessee [DOCK 50-564].

It would be desirable, at this point, to summarize general comments about the expected behavior of the fines and the consequences of this behavior. First, information assembled in this study indicates that the amount of fines produced per tonne of fuel processed is small, particularly material of small particle size, *i.e.*, below 100 mesh (149  $\mu\text{m}$ ). Some accumulation of fines in localized areas can be expected, and possibly, even ignition of the very finest material. However, ignition of hulls by the burning of fines is discounted; temperatures to 1600°C were reached in special zirconium powder burning tests and tubing sections only suffered surface oxidation. The consequences of any ignition are related to the kinds and amounts of combustible material in the vicinity of the burn zone, or the sensitivity of the localized region when exposed to relatively high temperatures for brief periods of time--on the order of a minute(s). Duration of the burn period is a complex function of (1) the availability of reactants (*e.g.*, free flow of air) and (2) the heat transfer (removal) characteristics of the burn zone. Burn-through of a vulnerable area such as a thin metal section in such a case is conceivable and should be considered in the plant design. Ignition of fines under water is completely discounted, even though references to under-water ignition have been found in the literature. The metal in the present case, nuclear-grade Zircaloy, is of high quality and is considered stable in comparison to the materials involved in past incidents.

With this as a background, the model flowsheet will be discussed.

### 1. Shearing and Dissolution

Shearing of whole fuel assemblies was selected as a reference step as opposed to the method proposed for the MFRP--namely, removal of end pieces\*, disassembly of the fuel bundles, and shearing of a few fuel elements at a time [DOCK-50-268]. Zircaloy fines are produced in either case, although the quantities of fines and size distribution for the two methods may differ. The main consideration is the distribution of the fines during the process, their retrieval, and their ultimate disposition.

The shear is provided with a water flushing system intended to minimize accumulation of fine material. Means of visual inspection to verify that this has been achieved is desirable. Even if ignition of a small amount of material were to occur, damage should be negligible since the metal shear sections are rather massive. Metal particles ignited during shearing would be expected to be quenched while traversing the conduit between the shear and the dissolver basket. Feather edges on individual tube sections might be fine enough to ignite but this would not cause ignition of the hull itself.

Fines which enter the dissolver basket are expected to partition, some staying with the hulls, while some fall or are carried out of the basket and end up with any undissolved fuel and fission products in the dissolver. Some of this material will be collected as a sludge in a feed clarification step. Cleanout of the remainder of this sludge from the dissolver will be required from time to time. These solids will all require monitoring for fuel content. Deactivation of the zirconium metal content by an oxidation step is proposed. This should facilitate disposal of this fraction and may improve the efficacy of ancillary treatments to remove residual fuel.

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\* Term includes nozzles, tie plates, end fittings, etc.

The importance of regular cleanout of radioactive sludge containing Zircaloy fines was clearly demonstrated in the report of a fire in a dissolver solution metering tank at the Windscale reprocessing plant in the United Kingdom. Although the fire appears to have been initiated when organic solvent was inadvertently admitted to the tank and was ignited by the radioactive sludge, the presence of Zircaloy fines and their subsequent ignition aggravated the situation [CMND].

## 2. Handling and Packaging of Hulls at the Reprocessing Site

Further (and final) separation of the fines from the hulls could be carried out by a coarse screening operation after the baskets containing the hulls (and fines) are retrieved from the dissolver and monitored for acceptable, residual fuel values. This separation could be carried out in air (with some chance of ignition occurring), or with a water flush, or completely under water. Ignition at this point might be economically undesirable if a burn-through of the screening equipment is possible. The problems of handling the contaminated water could be minimized by recycling and using a minimum volume in an effort to offset the disadvantages of the added liquid waste stream. The fines fraction should be oxidized as a means of deactivation as soon as practical and then be discarded with the hulls. No consideration of sand as a diluent or heat absorber in the hull containers is necessary in the present model if the fines have been treated in this manner.

Further handling of the hulls alone should not involve a pyrophoric hazard, once they are dumped into the waste containers and transported to their on-site storage location. Similarly, transportation of these containers to the Federal repository and any subsequent treatment (such as decontamination, compaction, etc.,) should be free of any ignition hazard, even after an extended period of storage. This assessment is based on the assumption that primary containers are of high integrity and that they prohibit the collection of water. Radiolysis would produce hydrogen so provisions should be made for sampling the gas space in the containers if any further handling of the hulls is contemplated.

## C. The Potential for Hulls Being a Pyrophoric Hazard During Accident Conditions

This section presents an evaluation of the possibility of pyrophoric behavior of hulls in the event of an accident during intersite shipment. Ideally, hulls in the absence of fines would not be pyrophoric regardless of the conditions encountered. This is particularly important when the hulls are outside a shielded, controlled facility, such as during shipment. It is difficult to select boundary conditions for the credible accident(s) and then define the conditions of temperature, pressure, and friction (scraping of surfaces, which would expose fresh, reactive metal) which the metal might encounter. If it can be shown that the accident conditions would cause no ignition and would be much less severe than the conditions under which hulls ignite, some conclusions might be drawn as to hull stability. In the absence of criteria for shipment of hull containers, the accident criteria for fuel shipping casks serve as guides; these include exposure to a 30-min fire (surface temperature 800°C), 30-ft drop tests, and water immersion [CFR]. Energies involved in recent fuel cask drop tests also serve as reference data; tests at speeds of 250 mph (110 m/sec) are in progress at Sandia [Shappert].

High energy, shock-impact tests\* were carried out directly on unirradiated Zircaloy tubing sections that simulated hulls instead of testing primary or secondary containers filled with material [Steindler]. The former was considered the most severe type of test. The total energies involved were similar to those encountered in some cask drop tests, but in our case the energy was impressed on a rather small sample (on the order of one kilogram of material rather than tonnes) and was expected to have considerable effect.

The tests involved impaction of an aluminum disk (impelled by an explosive charge), at two velocities, into a ~600-g sample of Zircaloy tubing sections. The sample material was confined both laterally and in the direction of impact in a heavy-wall pipe, 7.6-cm ID by 12.7-cm long with a wall thickness of 1.9 cm, mounted on a steel billet. Calculations made preliminary to tests indicated that the melting point of Zircaloy, about 1850°C, would be exceeded in tests at the higher velocity (2040 m/sec). Tests at even the lower velocity (790 m/sec) were considered quite severe compared to "ordinary accidents."

Tubing stock for the tests was hydrided and autoclaved and then chopped into 2.5-cm segments. One test was carried out on a compact (~1950 g) of segments of ~70% theoretical density while the other tests involved uncompacted material. Single tests also included fines (10% by weight) and sand (50% by weight) mixed with Zircaloy tubing sections.

Evidence of melting and ignition of individual tubing segments was observed in the tests at the higher velocity. The system was not instrumented to monitor peak temperatures. The lower velocity resulted only in compaction (mechanical deformation) of the individual tubing segments. When Zircaloy fines were added to the tubing, higher temperatures were sustained at the lower velocity, but no melting of tube segments was evident.

Tentative conclusions pending further evaluation of results follow:

1. Energy input sufficient to cause heatup of Zircaloy tubing segments to the melting point can result in ignition of the material but not necessarily sustained (complete) burning.
2. Energy input approximately equivalent to that achieved in drop tests on shipping casks results only in mechanical deformation (compaction) of individual tube segments.
3. Addition of a substantial quantity of zirconium powder in a test is not sufficient to achieve melting (or ignition) of the tubing. The fines were presumably converted to the oxide during the test that was carried out in air.

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\* The tests were devised and carried out by Shock Hydrodynamics, North Hollywood, California.

In summary, conceivable accidents appear unable to provide the energy needed to raise the temperature of Zircaloy hulls to the melting point; therefore hulls, *per se*, do not represent a pyrophoric hazard under accident conditions. Even the presence of a substantial quantity of fines does not alter this conclusion. Since shipments of hulls would involve both a heavy-wall primary container and a secondary container, these vessels, because of their design, would be likely to accommodate (absorb) much of the energy involved in shipment accidents.

#### VI. PROCESS OPTIONS THAT ENHANCE SAFETY

A review of information on pyrophoricity of zirconium with a view toward flowsheet options suggests that safety can be enhanced in several ways. In general, safety from a potential pyrophoric hazard would be advanced by compaction of the Zircaloy hull waste into a high-density form. Fines might be incorporated into the mass or separated. If separated, complete oxidation of the fines is recommended to eliminate any chance for ignition.

With densification, the thermal conductivity of the Zircaloy mass is increased significantly, an important consideration in the event any heat-generating reactions were to occur. Fission-product heat would be more readily dissipated, reducing the chance for hot spots to develop.

Compaction of the waste can be achieved with commercial hydraulic presses which would have to be modified because of the remote operation requirement. The applicability of commercial equipment is based on the work done routinely in handling nonradioactive scrap tubing at TWCA. Compaction tests on irradiated materials need to be done to establish whether the oxide films on the Zircaloy affect the nature (coherence) of the compact. Containers for storage of compacts would have to be designed.

A second option for compaction which may be simpler from a mechanical standpoint would be roll-compaction of the hull segments. This concept resembles an operation observed at TWCA, which produced "thick half-dollar" size wafers of zirconium powder. The operation on hull material would include separation of the fines for separate treatment (oxidation). Such an operation might also permit separation of dissimilar (metal) materials. Roll-compaction is considered to be essentially fully automatic. The product would be in a form suited to feeding to a packaging operation (*e.g.*, for storage) or other processing steps.

Compaction would not preclude decontamination of hulls prior to storage if schemes which destroy the metal matrix are to be used. The higher density of the compacted form permits increased loading in a fixed volume. On the other hand, decontamination schemes that attack only the metal surface, *e.g.*, additional exposure to nitric acid, would be ineffective after compaction.

Decontamination of the hulls is a process option at either the reprocessing plant or the waste repository; the choice of location is partly dependent upon the waste management flowsheet selected for hulls. Decontamination could eliminate pyrophoricity if the metallic zirconium is converted to a compound. The primary purpose of decontamination would be

to consolidate the TRU-bearing fraction into a small volume separate from the zirconium. For the zirconium fraction to be considered TRU-free, it should contain less than 10 nCi/g of waste. Therefore, the decontamination process must not only take into account the TRU elements associated with residual fuel, but also those present in the metal matrix itself (e.g., plutonium and daughters produced from the ppm levels of uranium impurity in nuclear-grade Zircaloy).

Separation of the zirconium by formation of the volatile  $ZrCl_4$  (described in Appendix C) shows promise as a means of consolidating the TRU-bearing fraction and completely eliminating the pyrophoricity potential [Steindler]. A subsequent option\* would be to react the tetrachloride with steam, as reported earlier [Holmes], to obtain the oxide, which is quite stable, for disposal as a waste. The TRU-bearing residue from the process could be mixed with the high-level waste or otherwise treated separately.

## VII. CONCLUSIONS

The Zircaloy hull waste stream, produced in the reprocessing of LWR oxide fuel by the chop-leach method, is considered a unique hazard requiring special handling and storage consideration. The hulls are potentially pyrophoric and, moreover, are contaminated with long-lived alpha-emitting transuranic nuclides as well as radioactive fission and neutron-activation products. On the basis of present information, the chop-leach step generates a relatively small but uncertain amount of Zircaloy fines, whose particle-size distribution is also uncertain. Spontaneous ignition of Zircaloy fines is a known hazard, yet the mechanisms are sometimes complex and frequently unknown. The behavior of fines has been studied with respect to physical parameters such as specific surface area and surface-to-volume ratios, but guideline values separating the safe and hazard domains are represented by a range of values. Furthermore, since no ignition work on actual hulls or other irradiated Zircaloy materials has been reported, conservatism should be exercised in the use of the information until a correspondence has been established between unirradiated and irradiated material.

The main concern regarding pyrophoricity is the potential for release of radioactivity that might endanger the safety of plant personnel and the public. Secondly, ignition might lead to equipment or plant damage, which in turn might represent a risk to personnel.

On the basis of the foregoing evaluation of the information in the literature and recent experimental work, it is concluded that a fraction of the fines produced in the chop-leach step is of small enough particle size to represent a modest pyrophoric risk. The hazard lies mainly in the propagation of any fire to other materials and the consequences of such fires. The "normal" amounts of such fines do not appear to have the

\*  $ZrCl_4$  is an intermediate form in the commercial fabrication of zirconium metal and hence could be used directly if recycle of zirconium becomes feasible; however, this needs to be evaluated for the impact of beta-emitting  $^{93}Zr$  ( $t_{1/2}$  of 9.5 E5 yrs) and other nuclides that might volatize with the  $ZrCl_4$  product.

potential for igniting hull segments. However, serious consequences could result from excessive accumulations of such material, and so disposal on a regular basis is recommended. Information available to date indicates that the melting of Zircaloy in tube segment form can result in ignition of the metal, but not necessarily sustained burning. This provides a reference point for evaluation of limiting energies in accident conditions but needs further study.

The potential for the hull stream being a pyrophoric hazard has been examined, using a hull management model. The reference flowsheet includes the chop-leach head-end without fuel element disassembly and a Federal repository for interim storage of hulls prior to their disposal. The Zircaloy fines produced by chopping are expected to be distributed between the fuel basket and the dissolver. It is recommended that fines be separated from the hulls after fuel dissolution and that fines be retrieved from the dissolver solution on a regular bases. Recovered fines should be deactivated by oxidation.

Recovery and treatment of the fines represents an area for further study. Pyrophoricity problems with the Zircaloy fines and hull segments can be mitigated, in general, by having the material submerged in water continually or, alternatively, keeping the material totally dry. Neither alternative may be feasible on a practical basis but safe practices can be developed with the use of small accumulation limits for fines.

Other process options exist that can enhance safety. Mechanical compaction of Zircaloy tubing and scrap is routine in the zirconium industry. Compaction improves heat transfer, which is desirable; it also provides considerable volume reduction, possibly of significant economic value. Transformation of elemental zirconium to a compound form would completely "deactivate" the pyrophoric hazard; *e.g.*, reactions to form volatile zirconium tetrachloride and then  $ZrO_2$  would accomplish this and may provide significant consolidation and volume reduction of the plutonium-bearing fraction. Appendix C of this report describes the procedures for and the results of a recently completed laboratory study on chlorination of Zircaloy cladding with  $HCl$  or  $Cl_2$ .

With the above-stated qualifications, hulls as produced in the chop-leach process are not considered a pyrophoric hazard in the absence of fines. However, since essentially all such information comes from work with unirradiated Zircaloy, work with actual hulls or at least irradiated Zircaloy materials should be done to confirm this conclusion.

#### VIII. ACKNOWLEDGMENTS

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## APPENDIX A

TABULATED DATA AND REFERENCES--THE PYROPHORICITY  
OF ZIRCONIUM: RESEARCH AND EVALUATIONAbbreviations Used in Evaluation Texts

amb	Ambient	mech	Mechanical
avg	Average	min	Minimum
chem	Chemical	prep	Preparation
combust	Combustion, Combustible	pres	Pressure
conc	Concentration	spon	Spontaneous
dia	Diameter	surf	Surface
expl	Explosion, Explosive	temp	Temperature
extr	Extrapolate	thk	Thick, Thickness
haz	Hazard, Hazardous	wt	Weight
ign	Ignition, Ignitable	yr	Year
irrad	Irradiation, Irradiated	Zr	Zirconium
max	Maximum	Zry	Zircaloy

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Study Area	References	Available Evaluation			
I.A.1. Effects of Storage Under Water	[Higgins]	Zry-2 wire samples submerged in H <sub>2</sub> O, ign. by resistance and total combust. measured			
		H <sub>2</sub> O	cover pres., psig oxygen	solution, temp. °C	% of wire burned
		pure	0	100	1
		oxygenated	1960	280	1
		oxygenated	1920	280	1
		oxygenated	1980	280	2
		oxygenated	1995	280	3
	[NFPA]	"Zr scrap chips or turnings completely immersed in water present a far lower fire risk than does the same scrap when exposed to the air in a wet, drained condition."			
	[AFP-44]	"---some expl. have occurred in cans containing Zr powders fully submerged in water."			
I.A.2 Effects of Storage Partially Immersed in Water	[Holt]	"---most dangerous conditions can occur when the moisture content lies between 3 and 16 w/o."			
	[Allison-1960]	"Scrap (Zr) finer than 20 mesh (0.084-cm dia) and coarser than 120 mesh (0.0125-cm dia) should be collected wet (under water),---. The amount of water should always be more than 25%---."			
	[TID-5365]	"Powders containing 16% or less moisture are considered particularly haz.---."			
I.A.3. Storage in Moist Air	[Guldner]	200-350°C, H <sub>2</sub> O gettered by Zr at same rate as O <sub>2</sub> ; above 350°C, H <sub>2</sub> is liberated.			
	[Higgins]	-0.054-in. dia wire in oxygenated H <sub>2</sub> O at 2000 psig and solution temp. at 280°C - no sustained burning after ign. -as above but 46% steam-54% O <sub>2</sub> , 100% wire burned. -0.106-in. dia wire, 100% O <sub>2</sub> , 13°C, 1015 psia, 100% burned. -as above but 96% O <sub>2</sub> , 4% steam, 132°C, 1045 psia, 100% burned. -as above but 50% O <sub>2</sub> , 50% steam, 286°C, 1915 psia, 100% burned. -as above but wire in H <sub>2</sub> O, 13°C, O <sub>2</sub> cover 1015 psia, 15.8 and 30% wire burned. -as above but 132°C, O <sub>2</sub> cover 1004 psia, 10.5% burned. -as above but 286°C, O <sub>2</sub> cover 915 psia, 0% burned.			

Study Area	References	Available Evaluation
I.A.3. (continued) Storage in Moist Air	[Litman]	-1/4-in. Zr barstock-ign and <u>not</u> quenched by H <sub>2</sub> O. -0.020-in. Zr strip-ign and quenched by H <sub>2</sub> O.
I.A.4.a. Effects of Metal-Water Reactions as a Function of Temperature - Hydrogen Evolution	none found	
I.A.4.b. Effects of Metal-Water Reactions as a Function of Temperature - Hydride Formation	none found	
I.A.4.c. Effects of Metal-Water Reactions as a Function of Temperature - Oxide Formation	[Barcch]	-Zr irrad for 3 yr 300°C 40 mg/dm <sup>2</sup> oxide wt gain 360°C 300 mg/dm <sup>2</sup> oxide wt gain 400°C 1000 mg/dm <sup>2</sup> oxide wt gain
	[Astker]	-Zr irrad for 1 yr at $3 \times 10^{13}$ n/cm <sup>2</sup> -sec 340°C 60 mg/dm <sup>2</sup> oxide wt gain
	[Bradhurst]	-Zr unirrad - extr to 3 yr 290°C 30-150 mg/dm <sup>2</sup> oxide wt gain
	[Burns]	-Zr irrad in steam @ $6.1 \times 10^{13}$ n/cm <sup>2</sup> extr to 3 yr 400°C 700 mg/dm <sup>2</sup> oxide wt gain
	[Page]	-Zry-2 VEWWR 3 yr @ 300°C 500 mg/dm <sup>2</sup> oxide wt gain Zry-4 in steam 3 yr @ 400°C 700 mg/dm <sup>2</sup> oxide wt gain Zry-4 in water 3 yr @ 316°C 50 mg/dm <sup>2</sup> oxide wt gain Dresden 3 yr @ 300°C 400-1000 mg/dm <sup>2</sup> oxide wt gain
I.A.4.d. Effects of Metal-Water Reactions as a Function of Temperature - Peroxide Formation	none found	
I.B. Effects of Liquids Other than Water (Chlorinated Solvents, Nitric Acid, Hydrofluoric Acid, Glycols, etc.)	none found	

Study Area	References	Available Evaluation		
I.C.1. Effects of Physical Characteristics - Particle Size	[Hartmann-1951, Jacobson]	particle size, $\mu\text{m}$		
		-44	$\sim 3$	$\sim 18$
		ign. air $^{\circ}\text{C}$	210	190
		ign. $\text{CO}_2$ $^{\circ}\text{C}$	560	620
		ign. $\text{N}_2$ $^{\circ}\text{C}$	530	790
		cloud $^{\circ}\text{C}$		20
		layer $^{\circ}\text{C}$		190
		expl conc, g/liter		0.045
		min ign, mJ		0.045
			15	120
	[Bulmer, Bulmer-1969]	particle configuration	assessment	
	-also see-	$\sim 60 \mu\text{m}$	-expl	
	[Allison, Allison-1960, Barnes, DeHollander-1956, TID-5365]	$>60$ , $\sim 850 \mu\text{m}$	-haz, fire risk	
		$<0.024\text{-cm thk}$	-easily ign	
		$>0.024$ , to $0.14\text{-cm thk}$	-ign with flame	
	[Hartmann]	Zr powders-		
		-ign temp, dust cloud - spon at room temp.		
		-min spark energy, dust cloud ign - 15 mJ.		
		-min expl conc - $0.040 \text{ oz}/\text{ft}^3$ .		
		-max expl pres - 50 psi.		
		-avg rate of pres rise - 1450 psi/sec.		
		-max rate of pres rise - 5000 psi/sec.		
		-min $\text{O}_2$ conc for spark ign - tests run in $\text{O}_2\text{-CO}_2$ mixtures.		
		Ign occurred in pure $\text{CO}_2$ .		

Study Area	References	Available Evaluation	
I.C.1. (continued) Effects of Physical Characteristics - Particle Size	[Jacobson, Littmar, Littmar-1961]	-dust cloud ign temp	
			fine Zr      coarse Zr
		in air	room temp      350°C
		in CO <sub>2</sub>	650°C      850°C
		in N <sub>2</sub>	850°C      850°C
		(max test temp was 850°C)	
		-dust layer ign temp	
			fine Zr      coarse Zr
		in air	190°C      300°C
		in CO <sub>2</sub>	620°C      710°C
		in N <sub>2</sub>	790°C      850°C
		(max test temp was 850°C)	
		-spark ign energies and min expl conc	
			fine Zr      coarse Zr
		cloud ign energy, mJ	15      12
		layer ign energy, mJ	0.0064      0.24
		min expl conc limit, oz/ft <sup>2</sup>	0.045      0.045
I.C.2. Effects of Physical Characteristics - Surface Area	[Schnizlein]	-T(ign) = 1070 - 208 log(A/m) A/m = cm <sup>2</sup> /g or specific area	38
	[Littman, Littman-1961, Bulmer]	-room temp ign tests	
			samp thk, in.      S/V ratio      specific area cm <sup>2</sup> /g      min O <sub>2</sub> press for ign, psi
		0.010      200      12.5      300	
		0.035      60      4.0      450	
		0.350      15      1.7      750	

Study Area	References	Available Evaluation		
I.C.2. (continued) Effects of Physical Characteristics - Surface Area	[Littman, Littman-1961, Bulmer]	-the rougher the Zr surf, the lower the ign temp. -surf temp test (0.5 x 3 x .035 in. strips), instantaneous 500 psi O <sub>2</sub> @ room temp	time, $\mu$ sec	surf temp, °C
		0 + 700	amb + 600	
		700 + 1200	600 + below amb	
		1200 + 2500	amb + 3200-3500 & ign.	
	[Levitz]	-surface in different forms		
		form	specific surf, cm <sup>2</sup> /g	S/V remarks
		sphere, 1- $\mu$ m dia	9200	60,000 pyrophoric
		sphere, 10- $\mu$ m dia	920	6,000 borderline
		Zr sponge sheet, 0.010-in. thk	100	~520 often pyrophoric
		sheet, 0.03-in. thk	12.7	82.7 borderline
		sheet, 0.03-in. thk	4.7	30.25 safe
I.C.3. Effects of Physical Characteristics - Surface Condition	[Schnizlein]	-in oxidation tests at 400, 500, and 600°C, the surf prep of 1 x 1.5 x 2 cm samples of Zr (mech and chem) had little influence on oxidation rates.		
	[Littman, Littman-1961, Porte, Porte-1960]	-oxidized vs. oxide-free - little or no difference in rate or conditions of ign/oxidation. -oxidized (black) vs. "as is" - as above. -oxidized vs. hydrided - as above. -oxidized vs. carbided - carbided considerably less susceptible to ign in O <sub>2</sub> .		
I.C.4. Effects of Physical Characteristics - Composition	[Goward]	-analysis of material from Y-12 "disaster"	conc in %	
		element	samp 1	samp 2
		carbon	0.5-2.6	0.24
		nitrogen	0.35	0.24
		oxygen	12.5	13.9
				samp 3
				21.4

Study Area	References	Available Evaluation																																																																		
I.C.4. (continued) Effects of Physical Characteristics - Composition	[Schnizlein, Porte, Porte-1960]	-alloying elements that <u>reduce</u> Zr oxidation rates Cu, Ni, Be, and Hf. -alloying elements that <u>increase</u> Zr oxidation rates Cr, Co, Pt, Fe, W, U, Mo, Pb, Nb, Ta, V, C, Ti, Al, Si, and Sn.																																																																		
	[Hericke-1958A, Mallett]	-addition of hydrogen (70 ppm initially to 16,000 ppm) increased ign reaction. Hydrided wire dark grey and very brittle. Wire lustrous and ductile after resistance heating ign tests. Increased oxidation of samples seemed to increase energies needed for ign (decrease in reaction potential).																																																																		
	[Porte, Porte-1960]	-oxidation data, binary alloys, 1000 days at 700°C, 200 mm O <sub>2</sub> press																																																																		
		<table> <thead> <tr> <th>Alloying Element</th><th>% in Zr</th><th>g O/cm<sup>2</sup></th></tr> </thead> <tbody> <tr> <td>Cu</td><td>1.08</td><td>2200</td></tr> <tr> <td>Be</td><td>2.09</td><td>2200</td></tr> <tr> <td>Ni</td><td>0.91</td><td>2300</td></tr> <tr> <td>pure Zr</td><td>----</td><td>2300</td></tr> <tr> <td>Hf</td><td>1.03</td><td>2400</td></tr> <tr> <td>Pt</td><td>1.08</td><td>2400</td></tr> <tr> <td>Cr</td><td>0.77</td><td>2600</td></tr> <tr> <td>Co</td><td>0.72</td><td>2750</td></tr> <tr> <td>Fe</td><td>1.09</td><td>3100</td></tr> <tr> <td>W</td><td>1.96</td><td>3100</td></tr> <tr> <td>U</td><td>3.52</td><td>3500</td></tr> <tr> <td>Mo</td><td>3.65</td><td>10,000</td></tr> <tr> <td>Pb</td><td>4.0</td><td>12,000</td></tr> <tr> <td>Nb</td><td>3.82</td><td>14,000</td></tr> <tr> <td>Y</td><td>3.88</td><td>15,000</td></tr> <tr> <td>Ta</td><td>3.54</td><td>20,000</td></tr> <tr> <td>C</td><td>3.72</td><td>30,000</td></tr> <tr> <td>Al</td><td>3.62</td><td>30,000</td></tr> <tr> <td>Si</td><td>3.60</td><td>30,000</td></tr> <tr> <td>Ti</td><td>4.16</td><td>35,000</td></tr> <tr> <td>Sn</td><td>3.60</td><td>50,000</td></tr> </tbody> </table>	Alloying Element	% in Zr	g O/cm <sup>2</sup>	Cu	1.08	2200	Be	2.09	2200	Ni	0.91	2300	pure Zr	----	2300	Hf	1.03	2400	Pt	1.08	2400	Cr	0.77	2600	Co	0.72	2750	Fe	1.09	3100	W	1.96	3100	U	3.52	3500	Mo	3.65	10,000	Pb	4.0	12,000	Nb	3.82	14,000	Y	3.88	15,000	Ta	3.54	20,000	C	3.72	30,000	Al	3.62	30,000	Si	3.60	30,000	Ti	4.16	35,000	Sn	3.60	50,000
Alloying Element	% in Zr	g O/cm <sup>2</sup>																																																																		
Cu	1.08	2200																																																																		
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Ti	4.16	35,000																																																																		
Sn	3.60	50,000																																																																		
I.D.1. Effects of Long-Term Exposure - Temperature	none found																																																																			
I.D.2. Effects of Long-Term Exposure - After Passivation (oxidized, nitrided, etc.)	none found																																																																			

Study Area	References	Available Evaluation
I.D.3. Effects of Long-Term Exposure - Contamination (fission products, actinides, corrosion products, etc.)	none found	
I.D.4. Effects of Long-Term Exposure - In Various Candidate Storage-Container Alloys (compatibility)	none found	
II.A.1. Material Response to Controlled Impact Forces Under Various Conditions	[Hericke, Herickes-1957]	-impact tests of various Zr, Zry-2, and Zry-3 scrap, chips, and turnings (fine, medium, coarse, and large coarse; 0.001 to 0.030 in. thk; 0.005 to 0.75 in. wide) no ign up to 750 kg-cm (54 ft-lb) impact in dry condition.
	[Littman]	-Zr strip immersed in liquid O <sub>2</sub> - 1730 kg-cm (125 ft-lb) was needed for ign. -in gaseous O <sub>2</sub> , no ign for impacts up to 1730 kg-cm.
II.A.2. Material Response to Controlled Friction Forces Under Various Conditions	[Hericke, Herickes-1957]	-friction tests of various Zr, Zry-2, and Zry-3 scrap, chips, and turnings (fine, medium, coarse, and large coarse; 0.01 to 0.030 in. thk; 0.005 to 0.75 in. wide) no ign. Sparking observed in 1 to 32% of pendulum swings "dry", 0 to 10% of swings "wet".
II.A.3. Material Response to High-Velocity Shock Forces from High-Explosive Charges	[Hericke-1958, Herickes-1958A]	Bench-scale shock-sensitivity tests - Tetranitromethylaniline expl shock generator <u>order of sensitivity</u> <u>material</u> 1      Zr powder, 7-9% water added. 2      Zr fine chips, 10% water added. 3      Zr sponge
II.B.1. Material Response to Static Charge Accumulation due to Handling (tumbling, pouring, washing, etc.)	none found	

Study Area	References	Available Evaluation		
II.B.2. Material Response to Static Discharge (minimum ignition energy)	[Hartmann-1951]	-spark ign data		
		form	dust cloud, mJ	dust layer, J
		Zr hydrided	100	64
		Zr fine	15	6.4
		Zr coarse	12	240
				expl conc min, oz/ft <sup>3</sup>
				0.12
				0.045
				0.045
II.C. Material Response to Flame and Combustion-Generated Heat	none found			
II.D.1. Material Response to Electrolytic Corrosion when Coupled with Various Other Metals	none found			
II.D.2. Material Response to Ignition Characteristics of Electrolytic Corrosion Products	none found			

## APPENDIX B

CALCULATED FISSION-PRODUCT, ACTINIDE, AND ACTIVATION  
PRODUCT INVENTORIES IN LWR ZIRCALOY CLADDING HULLSBases

- 0.1% fuel contamination of hull waste.
- 250 kg of hull waste per MTHM in spent fuel.

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Table B-1. Estimated Hull Waste  
Radioactive Inventory

Nuclide	Curies per Kilogram of Clad			
	FISSION PRODUCTS AND TRANSURANICS		ACTIVATION PRODUCTS	
	[AGNS] <sup>a</sup>	[Haug] <sup>b</sup>	[ORNL-4451] <sup>c</sup>	[Kee] <sup>d</sup>
scandium-46	-	-	5 E-3	5 E-3
chromium-51	-	-	3 EO	1 EO
manganese-54	-	-	7 E-1	6 E-1
iron-55	-	-	7 EO	6 EO
iron-59	-	-	9 E-2	6 E-2
cobalt-58	-	-	9 EO	8 EO
cobalt-60	-	-	2 E1	2 E1
nickel-59	-	-	2 E-2	1 E-2
nickel-63	-	-	2 EO	2 EO
strontium-89	3 E-1	4 E-1	2 E-2	2 E-2
strontium-90	3 E-1	3 E-1	-	-
yttrium-90	3 E-1	3 E-1	-	-
yttrium-91	7 E-1	6 E-1	6 E-2	7 E-2
zirconium-95	1 EO	1 EO	2 E1	2 E1
niobium-95m	3 E-2	2 E-2	-	-
niobium-95	2 EO	2 EO	4 E1	4 E1
ruthenium-103	4 E-1	4 E-1	-	-
rhodium-103m	4 E-1	4 E-1	-	-
ruthenium-106	2 EO	2 EO	-	-
rhodium-106	2 EO	2 EO	-	-
silver-110m	1 E-2	1 E-2	-	-
silver-110	nr <sup>e</sup>	1 E-3	-	-
tin-119m	1 E-2	4 E-5	7 E-2	6 E-2
tin-123	nr	2 E-2	nr	6 E1
antimony-124	-	-	1 E-2	1 E1
antimony-125	3 E-2	3 E-2	2 E-1	4 E1
tellurium-125m	9 E-3	1 E-2	7 E-2	2 E1
tellurium-127m	1 E-2	3 E-2	-	-
tellurium-127	1 E-2	2 E-2	-	-
tellurium-129m	2 E-2	1 E-2	-	-
tellurium-129	2 E-2	1 E-2	-	-
cesium-134	8 E-1	9 E-1	-	-
cesium-136	1 E-4	8 E-5	-	-
cesium-137	5 E-1	4 E-1	-	-
barium-137m	4 E-1	4 E-1	-	-
barium-140	1 E-3	2 E-3	-	-
lanthanum-140	2 E-3	2 E-3	-	-
cerium-141	3 E-1	2 E-1	-	-
cerium-144	3 EO	3 EO	-	-
praseodymium-144	3 EO	3 EO	-	-
praseodymium-143	2 E-3	3 E-3	-	-
neodymium-147	2 E-4	2 E-4	-	-
promethium-147	5 E-1	4 E-1	-	-
promethium-148m	nr	1 E-2	-	-

(Contd)

Table B-1. (Contd)

Nuclide	Curies per Kilogram of Clad			
	FISSION PRODUCTS AND TRANSURANICS		ACTIVATION PRODUCTS	
	[AGNS] <sup>a</sup>	[Haug] <sup>b</sup>	[ORNL-4451] <sup>c</sup>	[Kee] <sup>d</sup>
promethium-148	9 E-4	1 E-3	-	-
samarium-151	1 E-3	5 E-3	-	-
europlum-152	nr	5 E-5	-	-
europlum-154	3 E-2	3 E-2	-	-
europlum-155	1 E-2	3 E-2	-	-
europlum-156	nr	1 E-3	-	-
gadolinium-153	nr	1 E-4	-	-
terbium-160	6 E-4	1 E-3	-	-
neptunium-237	nr	4 E-4	-	-
neptunium-238	2 E-5	nr	-	-
neptunium-239	nr	2 E-2	-	-
plutonium-236	nr	3 E-4	-	-
plutonium-238	1 E-2	1 E-2	-	-
plutonium-239	1 E-3	1 E-3	-	-
plutonium-240	3 E-3	2 E-3	-	-
plutonium-241	6 E-1	4 E-1	-	-
americium-241	1 E-3	6 E-4	-	-
americium-242m	nr	4 E-5	-	-
americium-242	2 E-5	4 E-5	-	-
americium-243	nr	8 E-5	-	-
curium-242	2 E-1	8 E-2	-	-
curium-243	8 E-5	1 E-5	-	-
curium-244	1 E-2	1 E-2	-	-
curium-245	nr	4 E-4	-	-
<b>Total</b>	<b>2 E1</b>	<b>2 E1</b>	<b>1 E2</b>	<b>2 E2</b>

<sup>a</sup>35,000 MWd/MTU, 40 MW/MTU, @ 160-d cooling.

<sup>b</sup>34,000 MWd/MTU, 29.5 MW/MTU, @ 150-d cooling.

<sup>c</sup>33,000 MWd/MTU, 30 MW/MTU, @ 150-d cooling.

<sup>d</sup>25,000 MWd/MTU, 35 MW/MTU, @ 160-d cooling.

<sup>e</sup>Not reported.

## APPENDIX C

## SUPPLEMENTARY REPORT--CHLORINATION OF HULL WASTES\*

Zircaloy cladding segments constitute approximately 90 wt % of the hull waste stream that results from the chop-leach processing of light-water-reactor (LWR) oxide fuel. The remainder is mostly massive pieces of stainless steel and Inconel from the fuel assembly hardware. Also present are small amounts of transuranic elements (TRU), mainly from residual undissolved fuel but also from activation of the ~1-ppm tramp uranium in Zircaloy. Current Federal regulations [FEDREG] propose that TRU-contaminated wastes, namely, those containing >10 nCi/g, be packaged in a retrievable manner and consigned to a Federal repository for disposal. Untreated hull waste contains far in excess of this limit and occupies a relatively large volume. Consequently, considerable savings in packaging, interim storage, shipping, and burial costs can be realized if the volume can be reduced.

Volume reduction could be achieved by volatilization of zirconium, the major component (~98 wt %) of Zircaloys, away from the TRU elements. At about 400°C, Zircaloys readily react with such chlorinating agents as HCl or Cl<sub>2</sub> to produce ZrCl<sub>4</sub>, which sublimes at 331°C and 1 atm pressure. Conversion to ZrCl<sub>4</sub> would eliminate the hazard of zirconium pyrophoricity; however, it would be expedient to convert the difficult-to-handle ZrCl<sub>4</sub> to stable, solid ZrO<sub>2</sub> via pyrohydrolysis. Examination of the literature did not reveal any experimental measurements specifically addressed to the separability of ZrCl<sub>4</sub> from TRU elements during chlorination reactions with UO<sub>2</sub>-PuO<sub>2</sub>. However, considerable work has been done on head-end hydrochlorination processes for removing zirconium from U-Zr alloys [Ramaswami, Chilenskas] and on chlorination (Cl<sub>2</sub>, CCl<sub>4</sub>) volatility schemes for decontaminating UO<sub>2</sub>-PuO<sub>2</sub> and ThO<sub>2</sub>-UO<sub>2</sub> fuels from fission products [CONF]. To substantiate the feasibility of volatilizing TRU-free ZrCl<sub>4</sub>, a limited experimental investigation was undertaken. Mixtures of HCl/N<sub>2</sub> or Cl<sub>2</sub>/N<sub>2</sub> were reacted at ~400°C with solids representative of the hull waste, such as inactive or irradiated Zircaloy-2, unirradiated UO<sub>2</sub>-PuO<sub>2</sub>-Fissia, Inconel 718, and 304 stainless steel. Volatilized products were condensed at room temperature, dissolved in acid, and analyzed for plutonium and long-lived, gamma-emitting activation and fission products. The apparatus, procedures, and analytical data are detailed elsewhere [Ader, Ader-1977]. Overall results and conclusions are summarized below.

With HCl, the zirconium in Zircaloy was readily separable from TRU oxides. Less than 0.05 nCi of plutonium was found to accompany the 1- to 2-g portions of volatilized zirconium. Neptunium, americium, and curium are expected to behave similarly. TRU metals present in Zircaloy from transmutation of trace uranium will, in all likelihood, be converted to trichlorides, which are only slightly volatile at 400°C. The implication is that the zirconium form ultimately to be disposed of, e.g., ZrO<sub>2</sub>, would contain much less than 10 nCi of TRU elements per gram of solid and therefore not require disposal at a Federal repository.

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\* Work performed and reported by M. Ader, Chemical Engineering Division, ANL.

With  $\text{Cl}_2$ , about 10-20 nCi of plutonium volatilized with the 1- to 2-g portions of zirconium. Moreover, the volatility of plutonium seemed to be enhanced by  $\text{ZrCl}_4$  in the  $\text{Cl}_2$  stream, although the mechanism was not apparent. This effect was not observed in hydrochlorination experiments, presumably because  $\text{HCl}$  does not react with  $\text{UO}_2\text{-PuO}_2\text{-Fissia}$  at  $400^\circ\text{C}$  to yield the volatile plutonium species  $\text{PuCl}_4$ , whereas  $\text{Cl}_2$  does. With respect to LWR hull waste, treatment with  $\text{Cl}_2$  would produce  $\text{ZrCl}_4$  just at or slightly above the TRU limit of 10 nCi/g. Certainly, some of the plutonium in the Zircaloy matrix would be oxidized to  $\text{PuCl}_4$  and thus be transportable. Furthermore, there are disadvantages to  $\text{Cl}_2$  as compared with  $\text{HCl}$ , such as difficult control of reaction rate and temperature, and greater reactivity toward fission products, activation products, and materials of construction. In the experiments with irradiated Zircaloy-2, virtually none of the gamma emitters were volatilized with  $\text{HCl}$ , except for 1% of the antimony and 2% of the cesium. However, the reaction with  $\text{Cl}_2$  caused glowing hot spots on the surface of the irradiated Zircaloy, denoting localized temperatures greater than  $500^\circ\text{C}$ . As a result, substantially more radioactivity was volatilized, namely, 75% Sb, 15% Ru, 11% Cs, 8% Co, 3% Mn, and about 130 nCi Pu per gram of zirconium.

It should be realized that both mild and strong chlorinating agents will volatilize, in addition to normal zirconium, all the beta-active  $^{93}\text{Zr}$  ( $t_{1/2} = 9.5 \times 10^5$  y) induced in the Zircaloy cladding. Part of the tin, inactive and active (250-d  $^{119}\text{mSn}$ , 50-y  $^{121}\text{mSn}$ ), will also be transported. Consequently, the  $\text{ZrCl}_4$  condensate must be considered radioactive in any event, and any plans to salvage zirconium metal would have to be restricted to nuclear-industry use. Zirconium recovery would be particularly unattractive if  $\text{Cl}_2$  or some other strong chlorinating agent were used because numerous fission and activation products, beside those already mentioned, would volatilize. For example,  $\text{Cl}_2$  will volatilize all the inactive and active iron (2.7-y  $^{55}\text{Fe}$ ) in Zircaloy (but not necessarily in 304 SS or Inconel). Thus, the TRU-free volatilized-and-condensed fraction might require disposal as a highly radioactive material. Regardless of which chlorinating agent is used, the nonvolatile TRU-containing residue may present some disposal problems. If this residue is to be combined with other high-level wastes, e.g., as a glass or calcine, the massive pieces of unreacted stainless steel and Inconel would have to be sorted out. Also, it would be prudent to convert all chlorides in this residue to oxides, thereby precluding potential problems with moisture pickup and corrosion.

Operationally, a mild chlorinating agent like diluted  $\text{HCl}$  is preferable because the reaction is readily controlled and appears adaptable to simple, transpiration-like equipment and procedures; e.g.,  $\text{HCl}$  flow over heated trays containing the hull waste, and downstream condensation of  $\text{ZrCl}_4$ . The difficulty in controlling reaction rate and temperature that is encountered with strong chlorinating agents like  $\text{Cl}_2$  can probably be circumvented by using a fluidized bed, but entrainment of particles in the gas stream may prevent achieving the  $<10$  nCi/g limit. Finally, although there are economic and other incentives [Zima, Zima-1977] to reducing the volume of hull waste destined for a Federal repository, the costs and advantages of zirconium volatilization must be compared with competing processes. For example, compaction of hulls [Levitz] appears to be a simple procedure capable of yielding a volume reduction ( $\sim 70\%$ ) roughly comparable to that for hydrochlorination ( $\sim 85\%$ ). However, compaction has not been demonstrated with irradiated chop-leach-processed hulls, nor does it eliminate entirely the potential hazard of zirconium pyrophoricity.

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