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CHEMICAL DECONTAMINATION AND MELT DENSIFICATION

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CHEMICAL DECONTAMINATON AND MELT DENSIFICATION OF CHOP-LEACH FUEL HULLS

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In most commercial nuclear fuel reprocessing the spent UO_2-PuO_2 fuel material is dissolved from the sheared fuel bundle assembly with nitric acid. This process leaves the fragments of Zircaloy, stainless steel, and Inconel fuel bundle hardware as an undissolved residue. In total weight the hardware amounts to about 250 kg per metric ton of UO_2. As recovered from the dissolver the hardware residues are a high volume low density waste, about 1.1 kg/liter. The dissolution process residues are highly activated and substantially contaminated with long-lived transuranic elements. Without further processing fuel bundle residues constitute three-fourths of the high level TRU wastes requiring perpetual storage.

Battelle's Pacific Northwest Laboratories have undertaken for ERDA an evaluation of decontamination and melt densification of the chop-leach fuel bundle residues to minimize waste storage. Conceptually, melting of the high volume metal fragments to form a metal ingot will reduce storage requirements by a factor of six. Decontamination of the residues prior to melting to remove TRU element contamination is under study to the purpose that the treated metals will qualify for simpler, cheaper waste disposal categories.

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Our purpose in this presentation is to summarize our program on fuel bundle hardware decontamination and densification and the results of our inquiry into the nature of the waste stream with which we are dealing.

The Description of the Chop-Leach Fuel Bundle Residues

The head end waste stream consists of 2- to 5-cm pieces of fuel element cladding together with the end hardware and spacers, etc. The fuel cladding at the present time is Zircaloy. The end hardware, spacers and control rod guide tubes can be Inconel, Zircaloy or stainless steel.

Relative mass calculations of the various alloys in BWR and PWR fuel show 21% and 29% stainless steel plus Inconel, respectively. If the end hardware is excluded, this becomes 8% for the BWR and 19% for the PWR based on fuel designs for Brown's Ferry and Diablo Canyon reactor fuel designs. All of these materials are neutron irradiated. ?

The principal activation products remaining in the Zircaloy after 5 and 100 years cooling, as calculated by ORIGEN code, are ^{60}Co, ^{55}Fe, ^{125}Sb, ^{63}Ni, and ^{125m}Te. The total activity is 900 μCi/g Zr after 5 years and 18 μCi/g after 100 years. Zircaloy-2 and 4 usually contain trace amounts of uranium (~1 ppm) which will transmute to transuranic elements or fission during the irradiation. ? Calculations by ORIGEN code of the expected transuranic contamination uniformly dispersed in the metal from 1 ppm natural uranium contamination indicates the principal isotopes would be about

85 nCi/g of ^{241}Pu and 2 nCi/g ^{244}Cm in the Zircaloy after 5 years cooling. The balance of the transuranics would be less than 3 nCi/g total. A similar calculation of the transuranics generated in the Inconel and stainless steel parts could be made, however, a realistic estimate of the uranium and thorium impurities in these alloys has not yet been obtained. The zirconium cladding has been estimated to contain 30 to 60% of the fission product tritium.

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LWR fuel elements might have a corrosion product layer up to 50 microns thick in locations of maximum corrosion. Impurities circulating in the reactor (crud) deposit on fuel surfaces and can contain transuranics if the coolant is contaminated with uranium or plutonium from fuel ruptures.

The internal surface of the Zircaloy clad fuel develops an oxide layer of a few microns in thickness. The $(U,Pu)O_2$ fuel has been observed to adhere and perhaps react with this oxide layer. Estimates of residual $(U,Pu)O_2$ associated with the fuel cladding after leaching are usually stated as less than 0.1% of the charge.

Fuel contamination of the hulls will take place during the shearing. The shear blades undoubtedly become contaminated with fuel oxides which will partly be pressed into the surface of the sheared cladding and partly smeared into the cut end. To the extent these fuel particles have been smeared over by metal, they will not be available for surface removal. However, the irradiated Zircaloy will be less ductile than unirradiated material and any smearing will probably be very thin and easily accessible after a light etch.

Actinide Distribution in Chop-Leach Fuel Hulls

To decontaminate we need to know the distribution of Transuranic contamination associated with the hulls. ~~The selection of decontamination processes for fuel hulls requires an accurate knowledge of the distribution of transuranic contamination of the hull material.~~ A sample for analytical determination of t~~hese factors~~ distribution was obtained from a fuel rod (F-2[HQ]) exposed in Saxton Reactor about six years ago. Fuel composition was 6.6% PuO_2 in UO_2. A 0.6 cm piece of F-2[HQ] cladding was lightly surface abraded to remove corrosion product oxide and etched 30 seconds total in two nitric-hydrofluoride acid etch solutions. The decontaminated piece was moved to an uncontaminated area and etched 20 seconds more in two etches, and briefly leached in concentrated nitric for complete surface decontamination. Less than 25 microns was removed per surface in the total treatment sequence. The sample was then dissolved in etch solution in two approximately equal steps. One sample contained the dissolved outer and inner 0.014 cm surface layer and the other sample the residual 0.028 cm center. Radiation readings with survey instruments after decontamination showed no detectable α and 200 mR γ at contact. A second sample from the same section of fuel rod cladding (not abraded) was treated in 0.4 M ammonium oxalate - 0.16 M ammonium citrate - 0.1 M ammonium fluoride - 0.3 M hydrogen peroxide solution at 90°C for two hours and subsequently treated again under the same conditions with fresh solution for an additional two hours. The residual 1.1 cm

{0.4 ammonium oxalate, 0.16 ammonium citrate, 0.1 M ammonium fluoride and 0.3 M hydrogen peroxide adjusted to pH 5

piece of cladding was dissolved in 6 M HNO_3 - 1.7 M HF solution. An adjacent 0.43 cm piece of cladding which had been abraded and etched clean was dissolved to use as a correction for the previously dissolved piece with surface contamination. The results of these analytical determinations are shown in Table I. WHERE IN THE TEXT IS FIG. 1 & ACCOMPANYING NARRATIVE SUPPOSED TO GO?

Several small pieces of highly irradiated fuel exposed in a typical PWR were leached in a fuel dissolving operation (20 hours in nitric acid initial concentration 8 M) followed by 4 hours in 8 M HNO_3 at 99°C and by a water rinse. The cladding was further leached in a ~~0.4 M hydrogen perioxide~~ at 95°C for a total of 12 hours in five fresh 30 ml aliquots of solution. The extent of total alpha activity removal by the special leaching procedure is shown in ~~Figure~~ Table 1. This alpha activity is presumably fuel that has been incorporated with the zirconium dioxide corrosion product layer such that it is insoluble in nitric acid. The presence of fluoride in the leaching liquor causes it to dissolve a small quantity of ZrO_2 and promote the dissolution of trapped actinides.

The leached cladding was mechanically stripped of surface oxide at one end and a 0.67 cm piece of metal cut off. This piece was etched to remove surface contamination and then dissolved for analysis. A similar 0.96 cm piece from the other end was dissolved without treatment. A comparison of analyses normalized to internal surface area gives information on surface activity, activity in ZrO_2 layer and finally in base metal. These data show that 56% of total alpha activity was removed by leaching, 44% is in surface oxide and less than 0.02% is in base metal, See Table

An examination of the three potential decontamination methods, aqueous, molten salts, and melt fluxing processes showed the need for substantial development to achieve the desired objectives of high decontamination factor and minimization of the total waste stream. Review of the three processes from the standpoint of waste stream minimization and ease of operation shows that the major problem is removing the zirconium dioxide corrosion product layer.

Aqueous Decontamination Processes - It appears that a modified aqueous process, followed by melting, has the best promise of meeting the decontamination objectives. Treatment of zirconium dioxide corrosion films in HF gas at 550°C to 620°C produces films that are removable in dilute aqueous reagents. Metallography of samples of oxidized and unoxidized Zircaloy after HF treatment has shown that HF reacts with metal through film imperfections. The oxide is subsequently undercut and removed by the aqueous process. Metallography of a sample showing this laterally progressing reaction under the oxide is shown in Figure 2. No FIG. 2 HERE Studies of HF and Zircaloy reactions show an increasing rate with declining temperature in the 650°C to 500°C range (Figure 3). No FIG 3 The fact that there is minimal reaction of oxidized zirconium with HF at 500°C shows that the 550°C to 600°C temperature is apparently needed to produce film ~~imperfection~~ defects. HF can attack the metal through pores or cracks and spread laterally to push the oxide layer off the metal.

Fluoride containing gases such as boron trifluoride, carbontetrafluoride, hexafluoroethane, difluorodichloromethane are

~~Table I. Gross Alpha Count of Fuel Clad Samples~~

~~Σ 5 Leaches~~	~~1.89 · 10^7 D/M/cm^2~~ *
~~Residual Dissolution~~	~~1.47 · 10^7 D/M/cm^2~~
~~Base Metal After Surface Cleaning~~	~~4.2 10^3 D/M/cm^2~~

~~* It is assumed most alpha activity comes from the internal surface of the fuel clad and thus the values are stated per cm^2 of the fuel clad inner surface.~~

Examination of Table I will show that a substantial fraction of the residual TRU elements can be leached from the cladding surface. The isotopic analyses of the natural uranium in the base metal is consistent with the fuel burnup. No diffusion of TRU elements into the cladding base metal is observable. The low original uranium contamination of the high exposure PWR base metal at 0.3 ppm and very low thorium contamination (see low ^{233}U) resulted in more than 10 nCi/g of TRU elements even if one converts the ^{241}Pu to ^{2} Am. ~~Comparisons of the analytical results to the ORIGEN computer calculation have not yet been done.~~

The Decontamination Process

The chop-leach fuel hardware residue waste stream is contaminated by undissolved fuel particles, fuel-zirconium dioxide corrosion product layer interaction products, and irradiated uranium and thorium impurities in the original metal. Based on 0.1% of the original fuel as contamination on the hull waste stream, overall decontamination factors for the transuranium elements of 10^4 to 10^5 will be necessary to reduce transuranic element contamination below 10 nCi/g.

alternative fluoridizing agents. They are of especial interest because they do not produce water as a reaction product. The reaction of zirconium with water is an undesirable side reaction. Tests with CF_4 showed it to be nearly inert to Zircaloy and ZrO_2 at 550°C to 650°C. Boron trifluoride reacted with Zircaloy, but not as uniformly at HF. Dichlorodifluoromethane produced severe reaction with the metal which was not limited to a surface coating. C_2F_6 has not been tested yet. Mixtures of HF and BF_3 were similar in effect to HF alone.

The performance of the aqueous decontaminating solution was evaluated as a function of its constituent concentrations. No significant improvements were found over the original formulation of 0.4 M ammonium oxalate, 0.16 M ammonium citrate, 0.1 M ammonium fluoride and 0.3 M hydrogen peroxide adjusted to pH 5 at 90°C to 95°C.

A small section of the Saxton fuel cladding was treated at 600°C in HF for 30 minutes followed by 1.2 hours in an ammonium oxalate, citrate, fluoride, peroxide solution at 85°C to produce effective decontamination and film removal. Analyses of the stripping solution and the residual metal has verified that 99.7% of the α activity was removed by the HF-aqueous decontaminant treatment. The residual 0.3% of α activity compared with the 7 nCi/g found previously for the base metal indicates the process achieved as much decontamination as possible by surface removal alone.

In a second experiment a 2.5 cm piece of high exposure PWR Zircaloy fuel cladding was stripped chemically to simulate the results of the decontaminating process. The piece was weighed, then treated in a slow flow of argon and HF (about 50% HF) at 595°C to 625°C for 45 minutes. The treated piece was immersed in a 0.4 M ammonium oxalate - 0.16 M ammonium citrate - 0.1 M ammonium fluoride - 0.3 M hydrogen peroxide solution for 45 minutes at 90°C to 95°C. This process removed all of the visual oxide from the surface except for two (< 1 mm dia.) spots. An additional 45 minute treatment did not improve its visual appearance. Weight loss from the combined treatments corresponded to 3.2 g/dm^2 or 0.05 mm. The decontamination factor was greater than 10^4 with a substantial portion of the residual alpha activity in the base metal originating from irradiation of impurity uranium which is not available to surface decontamination. The residual alpha count in the base metal after surface decontamination was 21 nCi/g.

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

MELT DENSIFICATION

Melts in Induction Heated Graphite Crucibles - Consolidation of Zircaloy cladding hulls ~~by~~ melt~~ing~~ed with the stainless steel hardware in the fuel bundle could result in a single storable ingot having a minimum volume. By combining stainless steel with Zircaloy, low melting eutectic mixtures are formed which can lead to simplified melting processes.

Melting and cooling curves were determined for alloys of 10, 15, and 20% stainless steel in Zircaloy-2 in graphite crucibles heated by a resistance furnace. The objective of these experiments was to determine melting temperatures, the extent of crucible reactions, and the ingot quality.

Compositions in the range of 15 to 20% stainless steel can be melted and poured ~~in~~ from graphite at a temperature of 1300°C. Greater crucible wear and carbon pickup will occur in the 20% stainless steel range. Temperatures for melting in the 10% stainless steel range will be over 1400°C. The importance of oxygen contamination of the 15 to 20% melts was established in the first two runs where incomplete melting occurred even at 1400°C.

Of the chemical analyses on the melt stock and five of the six graphite melted heats the most significant are the carbon, hydrogen, oxygen and nitrogen values. A 250 ppm carbon level was the result of a high pouring temperature (1415°C). The melting of pure zirconium in graphite at temperatures of 1820°C to 1920°C will result in carbon contents as high as 3000 ppm. Hydrogen and oxygen showed little or no increase after melting. Nitrogen was slightly raised.

Inductoslag Melting Process - A demonstration of zirconium alloy cladding hull melting by the Inductoslag process was conducted at the U.S. Bureau of Mines, Albany, Oregon. The feed material for this melt was reject Zircaloy-4 fuel clad tubing chopped into one inch pieces and etched by the ammonium oxalate, citrate, fluoride, peroxide bath similar to that used in the decontamination process. The Inductoslag melting process uses an induction heated, split, water cooled copper crucible, as described by Clites and Beal. Melting takes place in a static, one-third atmospheric pressure helium. A pool of Zircaloy-4 and CaF_2 is melted on a "starting stub". ~~and~~ Charge materials ~~and~~, CaF_2 and Zircaloy tube sections, are vibratorily fed into the top of the crucible as the ingot is being extracted ~~out~~ from the bottom of the crucible. Approximately 41 kg (90 pounds) of simulated chop-leached cladding residues were melted into an ingot 10 cm ~~(4 inch)~~ diameter by ~ 75 cm ~~(30 inch)~~ long. Oxygen levels increased 36 to 430 ppm, but ~~was~~ were still within specification. These increases may have been due to a furnace leak in the hopper stirring shaft seal. Fluorine increased 9 to 19 ppm. ~~and~~ The increase (if any) in calcium was below the analytical sensitivity. Iron was below specification in the melt stock and remelting seems to have lowered it further. Silicon was also low. Hardness values were all within specification. Two billets from this ingot have been extruded into a rod 3.6 cm diamter by 97 cm long and a tube 3.8 cm OD by 2.5 cm ID by 198 cm long. The extruded 3.8 cm OD by 2.5 cm ID tube blank was reduced by a commercial cladding tube manufacturer to a finished size of 11.18 mm OD by 0.74 mm wall. ?

Samples of the etched recycled Zircaloy tubing were tested in a standard 400°C - 1500 psi autoclave test for 72 hours. The four samples gained weight between 16.2 and 17.2 mg/dm^2 ~~(16.5 mg/dm^2 average)~~ which is a normal weight gain. All surfaces were black and lustrous.

A 14 kg heat of Zircaloy-4 10 wt% 304 stainless steel - 5 wt% Inconel 718 was made by the Inductoslag process. Charge material consisted of chopped 2.5 cm long Zircaloy fuel cladding; 304L stainless steel rod sections; and 2.5 cm squares of 0.05 cm Inconel 718 sheet. Initial melting was attempted using the CaF_2 slag. For this low melting alloy an eutectic mixture of 48 wt% CaF_2 - 52 wt% MgF_2 (MP ~ 1000°C) was used successfully. Approximately seven hours of melting time was required to melt the 14 kg ingot. This was due to the long time required for the feed material to dissolve in the low temperature liquid. Increased power to the pool resulted in a larger pool volume with no ~~apparent~~ increase in pool temperature. The resulting crack-free ingot consisted of 5 to 10 wt% of unmelted Zircaloy, stainless steel, and Inconel "potted" in a matrix of solidified eutectic mixtures. Ingot hardness varied from 255 to 364 BHN. Surface finish and ingot soundness are adequate for direct storage.

A 34 kg heat (Number 460) consisting of three sections, (a) approximately 7 kg of alloy CF3 (308 stainless steel casting grade), (b) 14 kg of a 2 to 1 by weight mixture of CF3 and Inconel 718, and (c) 14 kg of pure Inconel 718 has been melted by the U.S. Bureau of Mines Inductoslag process. The pure CF3 (casting Grade 304) and the Inconel 718 are acceptable for storage or refabrication. The 67 wt% CF3 - 33 wt% Inconel 718 material is suitable for storage.

Our densification studies have emphasized melting of decontaminated (descaled) fuel hulls potentially suitable for non-TRU waste storage or for reuse in the case of a segregated Zircaloy product. ~~It is quite possible~~ Melting of uncleaned undescaled fuel hardware waste for the purpose of volume reduction alone may be an acceptable approach. Highly oxidized Zircaloy-4 was prepared and melted by the Inductoslag process to determine the ability of the process to densify uncleaned hulls. For charge material Zircaloy-4 clad tubing was pre-~~pe~~roxidized in four batches to the extent of 2900, 3500, 3700 and 7700 ppm. Subsequent chopping into 2.5 cm long pieces revealed the somewhat brittle nature of the material. Each batch was melted separately one on top of the other to produce a single 10 cm diameter ingot about 80 cm long. Melting characteristics ~~appeared to be~~ were nearly identical to those of clean hulls. The results of this experiment indicate that the Inductoslag process can melt without difficulty highly oxidized Zircaloy cladding.

Tritium Absorption and Storage in Zirconium Alloy Ingots - The melting of fuel hardware into ingots will release absorbed hydrogen and tritium. The approximately 100 ppm of hydrogen evolved ~~could~~ can be reabsorbed into another ingot. The absorption rate and equilibrium pressure of hydrogen over Zircaloy and Zr-(Fe, Ni, Cr) alloy ingots were studied at representative gas pressures and concentration. The absorption temperature was fixed high enough (700°C) that zirconium would dissolve its own oxides and nitrides which would otherwise impede absorption. A large temperature gradient over the length of the absorption specimen increases the capacity of the ingot for hydrogen while keeping equilibrium gas pressure down. Absorption rates for Zircaloy-2 and 85% Zircaloy-2 - 10% Type 304 stainless steel - 5% Inconel 718 with grit blasted surfaces were compared. In general the equilibrium pressures were controlled by the zirconium concentration. The rate of absorption favored the Zircaloy-2. The hydriding of the zirconium alloy always resulted in faster subsequent absorption rates even though the hydrogen was removed before the second absorption. This suggests the development of preferred path for absorption and diffusion. Both the alloy and Zircaloy-2 absorb hydrogen rapidly enough to be useful for storage of the hydrogen removed from the densified hulls.

Preliminary Conclusions

While the decontamination and melt densification studies have not yet progressed to hot cell demonstration with kilogram quantities of fuel residues, some initial conclusions are in order.

1) Uranium impurities at the level of 1 ppm or greater in the metal matrix lead~~s~~ to transuranic element concentration in irradiated fuel hardware in excess of 10 nanocuries/gram. In the United States this level of TRU defines a special category of waste storage. Composition specifications for uranium impurities in zirconium alloys for fuel applications should be reduced from 3.5 ppm to 0.3 ppm or less.

2) A promising aqueous decontamination method for zirconium alloy cladding sections has been developed in which oxidized surfaces are conditioned with HF prior to immersion in a solution of ammonium oxalite, ammonium citrite, ammonium fluoride, and hydrogen peroxide.

3) Feasibility of molten salt decontamination of oxidized Zircaloy has been demonstrated, but problems in salt dragout and excessive metal loss seem currently to favor use of the aqueous process described above. → This is only hinted at in body of report.

4) A low melting alloy of Zircaloy, stainless steel and Inconel corresponding to the occurrence of these alloys in current fuel designs was predicted and demonstrated. Satisfactory melting of this alloy has been achieved in induction heated graphite crucibles.

5) Segregated Zircaloy cladding sections have been directly melted by the Inductoslag process to yield a metal ingot suitable for storage. If the Zircaloy fuel stock is descaled prior to melting a high quality ingot is produced suitable for refabrication.

6) Both Zircaloy and Zircaloy-stainless steel-Inconel alloys are highly satisfactory getters and sinks for recovered tritium.

FUTURE DIRECTIONS OF THE PROGRAM

The PNL program is directed to hot cell demonstration at the kilogram level of the sources so far demonstrated cold or with very small samples. In support of hot cell demonstration, studies are currently underway to define secondary waste streams and methods for recovery and reuse or volume reduction of ~~the material~~ waste streams.

The recovery of fuel hardware in metallic form raises possibilities of reuse in applications where low level residual activity and minimum fabrication processing are acceptable. We will review fuel bundle disassembly prior to chop-leach as a method to reduce metal volumes charged to the dissolver and a method of upgrading the recovered product, e.g., high purity Zircaloy.

The economic feasibility of fuel hardware treatment needs analysis. It is our plan to compare costs of melt densification with and without decontamination with alternate residue processing and with direct perpetual storage of untreated residues.

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