Recycle of Zirconium from Used Nuclear Fuel Cladding:
A Major Element of Waste Reduction - 11336

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ABSTRACT

Feasibility tests were initiated to determine if the zirconium in commercial used nuclear fuel (UNF) cladding can be recovered in sufficient purity to permit re-use, and if the recovery process can be operated economically. Initial tests are being performed with unirradiated, non-radioactive samples of various types of Zircaloy materials that are used in UNF cladding to develop the recovery process and determine the degree of purification that can be obtained. Early results indicate that quantitative recovery can be accomplished and product contamination with alloy constituents can be controlled sufficiently to meet purification requirements. Future tests with actual radioactive UNF cladding are planned.

INTRODUCTION

The objective of current research is to determine the feasibility of recovery and recycle of zirconium from used fuel cladding wastes. Zircaloy cladding, which contains 98+% of hafnium-free zirconium, is the second largest mass, on average ~25 wt %, of the components in used U.S. light-water-reactor fuel assemblies [1]. Therefore, recovery and recycle of the zirconium would enable a large reduction in geologic waste disposal for advanced fuel cycles. Current practice is to compact [2] or grout the cladding waste and store it for subsequent disposal in a geologic repository.

This paper describes results of initial tests being performed with unirradiated, non-radioactive samples of various types of Zircaloy materials that are used in UNF cladding to develop the recovery process and determine the degree of purification that can be obtained. Future tests with actual radioactive UNF cladding are planned.

POTENTIAL BENEFITS

To put the potential benefits of recovery and recycle of zirconium in further perspective, UNF generation in the U.S. in the next ~50 years is expected to be ~3,000 MT/year (heavy metal) and, at that capacity, the cladding waste production rate would contain ~1,000 MT/year of zirconium (assuming a recycle plant would process UNF from the current 70% PWR–30% BWR mix of UNF [1]. Since the value of hafnium-free zirconium used by the U.S. nuclear industry ranges between $40 and $80 per kilogram, the potential material cost savings could be more than $40M/year. Further economic benefit would result from the reduction of geologic waste disposal costs.

Currently used Zircaloy cladding contains zirconium with natural abundance isotopic composition, and UNF cladding contains one radioactive isotope, zirconium-93, formed by neutron capture on natural zirconium-92 during irradiation. Therefore, the potentially recovered zirconium would be radioactive; however, the zirconium-93 has a low specific activity (half-life is 1.5 million years) and only a weak beta emission. Therefore, the recycled zirconium would have low radioactivity if it can be decontaminated from other fission and activation product elements. This is a goal of the recovery process.

Moreover, successful recovery and reuse of the zirconium in UNF cladding could enable the economic use of enriched zirconium-90 in future cladding manufacture, and thereby add the potential benefit of improved reactor performance.

USED NUCLEAR FUEL (UNF) HEAD-END PROCESSING

The zirconium recovery process would be integrated into the advanced fuel cycle head-end process steps (Fig. 1) for treatment of UNF assemblies, following the voloxidation process, a dry pyrochemical step which is planned for use to remove volatile activation and fission products, including xenon, krypton, tritium, carbon-14, and iodine [3].
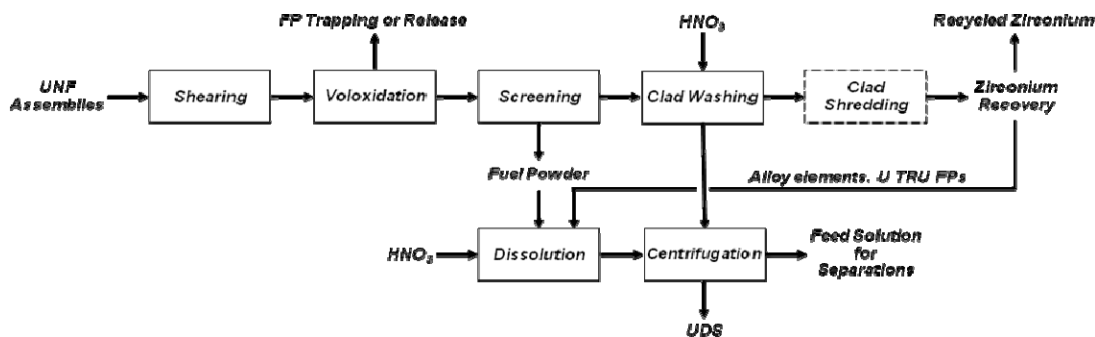

Fig. 1. Typical head-end operations.

After the voloxidation process step, the fuel components are present in the form of finely divided powder that can be separated easily by screening from the empty, sheared cladding hulls.

Recent tests at Oak Ridge National Laboratory (ORNL) with actual used fuel rods (Table I) have shown that most of the residual fuel powder remaining on the cladding hulls after screening can be removed by

Table I. Residual Contamination after UNF Clad Washing.

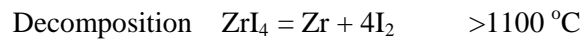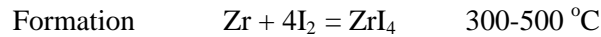| Element	Removed by cladding wash (Wt.% of UNF)	Remaining in washed clad (Wt.% of UNF)	Reduction factor	Residual clad contamination (ppm)
U	0.6	0.0037	162	100
Pu	0.3	0.013	23	6
Am	0.2	0.013	15	0.6

hull washing with nitric acid. However, the washed hulls still would contain residual contamination sufficient to prevent disposal of the clad as low-level waste. The residual contamination would be removed during the zirconium recovery process along with the alloying constituents and returned to the UNF reprocessing plant for disposal together with other radioactive wastes.

A process step for clad shredding may be needed to increase the surface area and thereby the efficiency of the zirconium recovery step. In addition, previous tests have shown that approximately half of the tritium remains within the cladding hulls [4]. Therefore, removal and capture of residual tritium will be included during radioactive process development studies that are planned.

PROCESS FOR ZIRCONIUM RECOVERY FROM CLADDING

Initially, nonradioactive tests are being made to determine the feasibility of zirconium recovery. The nonradioactive feasibility studies are being done by experts from Chemical Vapor Metal Refining, Inc. (CVMR), at its R&D laboratories. These studies can demonstrate refining of metals on a scale between 10 g and 10 kg. CVMR is participating in this work as a subcontractor to ORNL to provide expertise in the adaptation, process design, testing, and scale-up of the "hot wire"process that was developed by van Arkel and de Boer [5].

The proposed metal-refining process (Fig. 2) consists of two steps. As indicated in the following chemical reactions, in the first step, zirconium in the cladding is reacted with elemental iodine at 300–500°C to form volatile ZrI_4, which, in the second step, is then decomposed at >1100°C.

$$\text{Formation} \qquad Zr + 4I_2 = ZrI_4 \qquad 300\text{-}500 \ ^oC$$

$$\text{Decomposition} \quad ZrI_4 = Zr + 4I_2 \qquad >1100 \ ^oC$$

Nonvolatile residues, including radioactive contamination, would be returned to the UNF processing plant for disposal with other radioactive wastes.
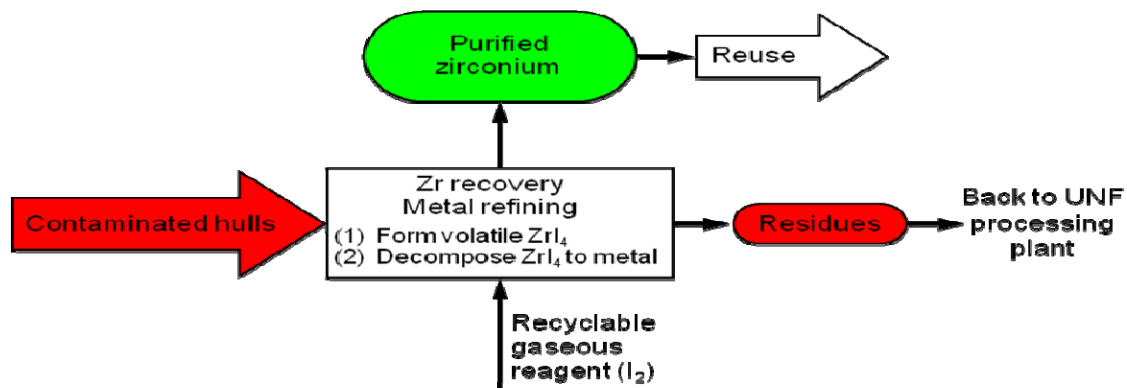

Fig. 2. Zirconium recovery from cladding.

Compositions of the alloying elements and other constituents of three types of Zircaloy that are representative of those in UNF cladding are shown in Table II. Samples of these three types are being used in the non-radioactive zirconium recovery tests. The samples of Zircaloy-2, Zircaloy-4, and high-niobium-content Zircaloy were obtained in ingot form from Allegheny Technologies, Inc., Wah-Chang Division, and were cut at ORNL into machine turnings to simulate shredded hulls. Also, in-stock samples of 3/8-in.-diam. Zircaloy-2 tubing were cut at ORNL into 1/4-in. lengths and sent to CVMR for initial testing.

Table II. Representative Composition (ppm) of Zircaloy Samples.

Element	Zircaloy-2	Zircaloy-4	High-Nb Zircaloy
Sn	14,200	12,900	<35
Nb	<50	<50	10,100
Fe	1,720	2,140	400
Cr	1,020	1,110	<50
Ni	690	<35	<35
O	1,320	1,180	1,370
C	130	140	47
N	42	39	33
Si	91	96	<25
Al	45	54	41

The components that are potentially volatilized along with ZrI_4 are shown in Table III, based on reference data supplied by CVMR in its design report.

Table III. Pertinent Reference Information .

Compound	Boiling point (°C)	Melting point (°C)	Vapor pressure at 431°C (bar)	Volatilization conditions
ZrI_4	431		1.004	$Zr + I_2$ at >500°C
ZrI_2				Not stable at >430°C
SnI_4	341*	144	22.84	$Sn + I_2$ at >150°C
SnI_2	320	720	0.0059	
NbI_5	347	327		$Nb + I_2$ at high I_2 pressure
NbI_3	450–500			Decomposition of NbI_5
NbI_2			Very Low	Decomposition of NbI_3 in presence of reducing agent
FeI_2	609	935	1.716	$Fe + I_2$ at >300°C
I_2	184	114		

*Sublimes at 180°C

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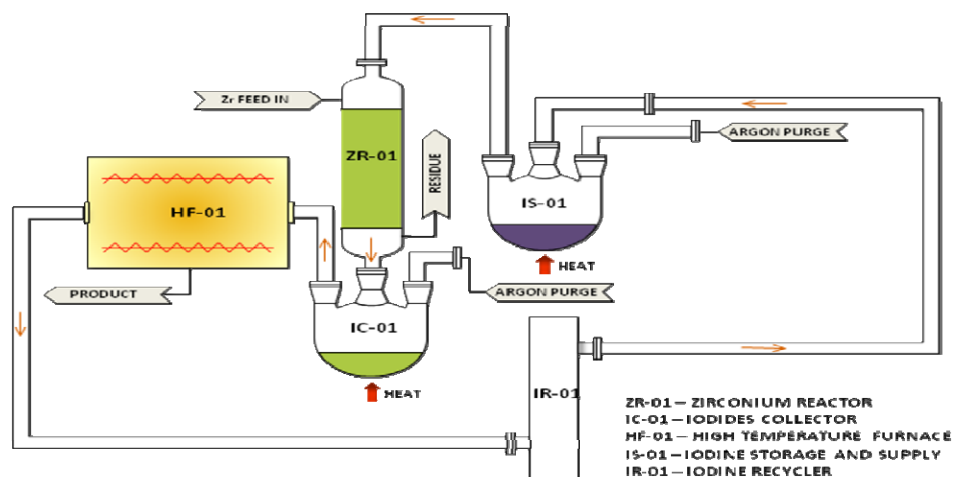The initial test apparatus set up by CVMR is illustrated in Fig. 3.

Fig. 3. Zirconium recovery apparatus.

In this apparatus, which was constructed of glassware and quartz, ~50–100 g of Zircaloy hulls or shredded Zircaloy was placed in the ZrI_4 formation reactor, ZR-01, which was heated to >500°C. Elemental iodine was heated to 150 ^{o}C in the iodine supply tank, IS-01, and dilute iodine vapor was transferred from IS-01 via an argon gas stream, flowing downflow through the ZrI_4 formation reactor, ZR-01. Intermediate-product ZrI_4 was collected in tank IC-01 and sampled for purity determination. The ZrI_4 was then re-vaporized and transferred by means of an argon stream to the decomposition reactor, HF-01, which was operated at a temperature of ~1170°C to produce zirconium metal foil product.

INITIAL TEST RESULTS

Table IV. Feasibility Test Summary

Test No.	Zircaloy Type	ZrI_4 Formation Reactor	I_2 Feed	ZrI_4 Yield (%)	Product* Contamination % of Feed			Additive
					Sn	Nb	Fe	
1	1:2 Mix High Nb/Zr-2 Tubes	Quartz Column	Gas in Ar	3%	^100%	0	**	xs I_2
2	1:2 Mix High Nb/Zr-2 Tubes	Quartz Column	Solid increments	~40%	^100%	2.4%	**	None
3	High Nb Shreds	SS-Sealed	Solid	80-100%	----	33%	**	xs Zr
4	High Nb Shreds	SS-Sealed	Solid	100%	----	0	**	Reducing Agent
5	Zr.4 Shreds	SS-Sealed	Solid	94%	0	----	**	None
6	High Nb/Zr-2 Tubes	SS-Sealed	Solid	100%	0	3%	**	Reducing Agent
7	High Nb/Zr-2 Tubes	SS-Sealed	Solid	***	***	***	***	xs Reducing Agent

*Intermediate product (ZrI_4) in Test #1 and #2; Zr metal product in Tests 3-6.
** Iron contamination measurement was higher than feed.
*** Analysis in progress.

A total of seven experimental tests have been made. Results are summarized in Table IV. The iron contaminant measured in both the intermediate product (ZrI_4) and the Zr metal product is, as yet, an unresolved anomaly.

The initial test, using a mixture of high niobium Zircaloy and Zircaloy-2 tube samples in the test apparatus configuration shown in Fig. 3, was not successful because the I_2 vapor, diluted in argon gas, was not sufficiently concentrated to sustain an efficient reaction rate, even at temperature exceeding 500^oC. Below that temperature, most of the I_2 vapor passed through the formation reactor, ZR-01, without reaction. The yield of ZrI_4 was only 3%.

The difficulty was partially rectified in the second test in which solid I_2 was added directly to the formation reactor, ZR-01, in several increments. By this means, the conversion to ZrI_4 was increased to ~40%. In more recent tests, the solid iodine and Zircaloy metal were initially charged to a sealed stainless steel reactor. Heating was applied to raise the temperature, and an exothermic reaction was observed to begin at ~300^oC. The reactor was then heated to 450^oC and held for 6 h to ensure completion of the iodide formation. Measured conversions to ZrI_4 were increased to 90-100%. While the sealed reactor configuration tests showed high conversion is possible, use of a pressurized reactor is not acceptable for commercial scale operations and may not be necessary if a more concentrated I_2 feed stream can be designed. Therefore, reactor and feed supply re-designs are required.

Following the latter tests in which a high conversion to ZrI_4 was obtained, the formation reactor was connected to the decomposition reactor, and the iodide was transferred by means of an argon purge at ~350°C. Zirconium metal foil was produced in the decomposition reactor and analyzed for impurity content by means of X-ray fluorescence (XRF). A key finding was that suppression of volatile niobium requires addition of a reducing agent to the iodide formation reactor feed.

Results of tests made using Zircaloy-2 or Zircaloy-4 as feed material showed the behavior of the tin alloy. Although volatile SnI_4 was produced in essentially quantitative yield, the final zirconium metal product did not contain a measurable amount of tin. Thus, the SnI_4 did not decompose and will need to be removed from the iodine by distillation to allow recycle of the iodine.

CONCLUSIONS AND FUTURE WORK

Feasibility test results obtained have confirmed that zirconium can be recovered in high yield and with sufficient purification from the key non-radioactive impurities, tin and niobium. Continued research is planned to resolve the issues of reactor and I_2 feed system design and to determine appropriate materials of construction for a commercial scale recovery system. Design of a test apparatus for verification tests on actual radioactive UNF cladding is in progress.

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