# A Study on the Radio-activity Reduction Method for the Decladding Hull

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## ABSTRACT

The cladding materials remaining after reprocessing process of the nuclear fuel, generally called as hulls, are classified as a high-level radioactive waste. They are usually packaged in the container for disposal after being compacted, melted, or solidified into the matrix. The efforts to fabricate a better ingot for a more favorable disposal to the environment have failed due to the technical difficulties encountered in the chemical decontamination method. In the early 1990s, the accumulation of radio-chemical data on hulls and the advent of new technology such as a laser or plasma have made the pre-treatment of the hulls more efficient.

This paper summarizes the information regarding the radio-chemical analysis of the hull through a literature survey and determines the characteristics of the hull and depth profile of the radio-nuclides within the hull thickness. The feasibility study was carried out to evaluate the reduction of the radioactivity by peeling off the surface of the hull with the application of laser technology.

## 1. INTRODUCTION

The spent PWR nuclear fuels are stored at the storage pool located in the nuclear power

plant until they are reprocessed. During the reprocessing of spent PWR fuel, the fuel rods are chopped into pieces of about 3~5 cm long. The chopped fuel rods(rod cuts) are dissolved in the boiling nitric acid. The dissolved uranium and plutonium are reclaimed by separation and purification processes. This is, what is called, a wet reprocessing of nuclear fuel[1].

On the other hand, the spent PWR fuel rod are cut into pieces of 30cm long during DUPIC fuel fabrication process. The uranium powder are separated from the cladding materials through the OREOX process[2].

The cladding materials remaining after reprocessing process of the nuclear fuels are generally called as hulls. Because the hulls are contaminated with fission products, activation products and transuranic radio-nuclides, they are categorized as a high level radioactive waste in either case.

Although the reprocessing of nuclear fuels are restricted by national policy, the nuclear fuels that are stored in the pool without any treatment have to be treated someday because of the tough storage space problem. It is, therefore, essential to establish possible technology for the treatment of hulls in the event that the technology is needed.

The hulls are usually packaged in the container for disposal after being compacted, melted, or solidified into the matrix. Their ultimate disposal may be complicated by the presence of fission products, activation products and α- actinides. Removing the long-lived actinides elements from cladding hulls reduces the volume of TRU waste that requires special handling and treatment, thereby reduces the disposal cost[3]. The efforts to fabricate a better ingot for a more favorable disposal to the environment have failed due to the technical difficulties encountered in the chemical decontamination method. In the early 1990s, the accumulation of radio-chemical data on hulls with the technology development have made the pre-treatment of the hulls more efficient.

This paper summarizes the information regarding the radio-chemical analysis of the hull through a literature survey and determines the characteristics of the hull and depth profile of the radio-nuclides within the hull thickness. The feasibility study was carried out to evaluate the reduction of the radioactivity by peeling off the surface of the hull with the application of laser technology.

## 2. RADIO-CHEMICAL CHARACTERISTICS OF HULLS ORIGINATING FROM THE WET REPROCESSING PROCESS BY RESTANI ET AL.[4]

### 2.1 Dose Rate and Measurement of Radioactivity

The Hulls originated from a wet reprocessing process of spent PWR fuel rods whose burn-up was 30,000 MWD/MTU and cooling time was 5 years. The dose rate and radioactivity are shown in Table 1. The γ radio-activities for the hull are measured with a high purity Ge detector. The γ dose rate at a distance of 0.5m was about 10~50mR/hr(average 25±8mR/hr). The species of the fission products are identified from the analysis of the gamma ray spectrum obtained by the gamma spectrometry measurement system. The β and γ radioactivity from the hulls are dominated by Sb-125 from the alloying element tin.

### 2.2 Actinide Analysis of Zircaloy Hulls

A specimen of the zircaloy-4 hull is dissolved in 3M HNO3/2M HF. The contents of actinides are obtained by the isotope dilution analysis method. The results are shown in Table 2. Table 2 shows that the average contents of uranium and plutonium are 1,130mg U/kg Zry and 13.6 mg Pu/kg Zry, respectively. In the mean time, the result of the α- autoradiography to

evaluate the qualitative TRU distribution shows that the contents of uranium and plutonium are 380~2130mg U/kg Zry and 6.3~25.3 mg Pu/kg Zry, respectively.

### 2.3 SIMS Analysis of Zircaloy Hulls

The concentration depth profile of the radio-nuclides is analyzed with a shieled secondary ion mass spectrometer by Restani. The SIMS analysis shows that uranium adheres mainly to the zircaloy surface and that the concentration in the oxide layer drops sharply. The fission product penetrates at a considerable distance to about 10 μm as recoil particles. The lightest element, Sr-88, penetrates the farthest distance of 12 μm.

## 3. RADIO-CHEMICAL CHARACTERISTICS OF THE HULLS ORIGINATING FROM THE DUPIC FUEL FABRICATION PROCESS

### 3.1. Hulls from the DUPIC Fuel Fabrication Process[2]

The concept of DUPIC(Direct Use of spent PWR fuel in CANDU reactors) technology is to manufacture nuclear fuel for CANDU reactors using spent PWR fuel. DUPIC fuel fabrication consists of de-cladding, powder preparation, pelletizing, and fuel element manufacturing processes. The hulls originated from a DUPIC fuel fabrication process with the spent PWR fuel rods whose burn-up is 32,000 MWD/MTU and cooling time is 15 years.

### 3.2. Oxide Layer

The oxide layer formed on the surface of the hull acts as a protective barrier to corrosion. An internal oxide layer forms due to the reaction with the $UO_2$ nuclear fuel during the

irradiation, while the outside one forms due to the reaction with the reactor coolant. As a result, the thickness of the outside oxide layer is thicker than that of the inside layer. Sometimes, α-nuclides such as Pu and U may be implanted inside the oxide layer due to the collision with heavy fission fragments. The amount of the α-nuclides near the hull surface decreases exponentially with a maximum penetration depth of 1 μm. Oxygen potential was measured to find the oxide layer thickness and is shown in Fig. 1.

In Fig. 1, it is known that fission products, especially zirconium, exist as an oxide form, because the oxygen potential increases to the depth of 3 μm from the maximum peak of plutonium. It is reported that the outside layer of the hull surface amounts to 6.5~11.7 μm while the inside layer is 1~2 μm for the hull generated from the wet reprocessing process.

### 3.3. EPMA analysis for the inside Surface of the Hull

The 1 cm long EPMA sample was prepared by the cutting, washing and compacting of the hull. The result of the EPMA analysis is shown in Fig. 2. It is found that most of the radio-nuclides are distributed within the thickness of 10 μm . Zr is the major element whose composition is equal to 98.9%. Other elements are equal to 1.1%.

## 4. FEASIBILITY OF THE RADIOACTIVITY REDUCTION BY PEELING-OFF THE HULL SURFACE

### 4.1. Inherent Radioactivity Arising from U Impurity in Zirconium Metal

Transuranic nuclides arise from U impurities that are distributed uniformly throughout the zirconium metal. The radioacivity due to these transuranic nuclides are calculated by ORIGEN II code and the result are shown in Table3. Table 3 shows that the use of Zircaloy clad fuel containing 3.5ppm of uranium in the cladding leads to the 3~8nCi/g

radioactivity rise, which is less than a TRU criteria of 100nCi/g. Therefore, hulls are not categorized as a TRU waste by the transuranic nuclides alone arising from U impurities. This indicates that the hulls can be converted to non-TRU waste by removing other actinides that exist in the hull surface by peeling- off the hull surface.

### 4.2. Radioactivity Reduction

In the wet reprocessing of the spent PWR fuel rod, the radioactivity due to the material remaining on the hull surface is shown in Table 2. Distribution pattern of the radio-nuclides from the hull surface to the depth are as follows. Fission products such as Cs-137, Sr-88, Ba-138, La-139, Eu-154 are distributed within a 10~15 μm thickness from the hull surface. 99.5% of the α-nuclides such as Pu and U are distributed within a 5 μm from the hull surface and decrease exponentially from 5 to 15μm. The other 0.5% of the α-nuclides exist within a hull deeper than 20 μm.

Accordingly if the hull surface is peeled off to a maximum of 20 μm, the total radioactivity will be greatly reduced due to the elimination of the fission products and α-nuclides. The total radioactivity from the hull surface is anticipated to be TR=0.000000+6.65X).005=0.03325 mCi/kg Zry, which is below the TRU waste criteria of 0.1 mCi/kg Zry(=100nCi/g) of Zry.

### 4.3. Heat Generation from the Hull

TRU waste criteria is 2kw/$m^3$ from the heat generation perspective. Heat generation of 2kw/$m^3$ is equal to about 0.31 W/kg, assuming 100% of ingot density. The thermal characteristic of the hull is calculated by ORIGENII code and the result is shown in Table 4.

Table 4 shows the heat generation will naturally fall down to 0.0192W/kg at 5 years from discharge, which is far below TRU waste criteria of 0.31 W/kg. It is understood that no additional effort is needed to reduce the heat generation below the TRU waste criteria of 0.31 W/kg because the heat generation drops to below 1/10,000 of the TRU waste criteria after the average storage period of 30 years.

### 4.4. Peeling-off a Zircaloy-4 Cladding Hull

The inactive zircaloy-4 cladding hull is peeled off by applying a laser technique. The result is shown in Fig. 3. It is understood that it is quite feasible to peel off the hull surface to 10~150μm.

## 5. CONCLUSIONS

With about a 20μm peeling-off of the hull surface, the total radioactivity from the hull surface falls down to 0.03325 mCi/kg of Zry, which is far below the TRU waste criteria of 0.1 mCi/kg of Zry. After 5 years from the discharge, the heat generation from the hull drops to 0.0192W/kg which is well below the TRU waste criteria of 0.31W/kg. The 20μm peeling-off of the hull surface is feasible by applying a laser technique. It is, therefore, possible that the hull, currently a high level radioactive waste, can be converted to a non-TRU waste by a 20μm peeling-off of the hull surface.

## ACKNOWLEDGEMENT

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## REFERENCES


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**Table 1. Mean activities of fission and activation products and α-nuclides in Zircaloy-4 hulls from reprocessing of a spent fuel element. (cooling period: 5years, burn-up: 30,000MWd/tU)**

| Fission Products | | | Activation Products | | | α-nuclides | |
|---|---|---|---|---|---|---|---|
| nuclide | Radio-activity (mci/kg-Zry) | Half life | nuclide | Radio-activity (mci/kg-Zry) | Half life | nuclide | Radio-activity (mci/kg-Zry) |
| Cs-137 | 542 | 30.1 y | Sb-125 | 760 | 2.70 y | Pu(t) | 4.51 |
| Ru-106 | 458 | 372 d | Co-60 | 64 | 5.27 y | Cm-244 | 1.24 |
| Cs-134 | 162 | 2.10 y | Mn-54 | 3.4 | 312 d | Am-241 | 0.90 |
| Ce-144 | 70 | 285 d | | | | | |
| Eu-154 | 21 | 8.80 y | | | | | |
| total | 1253 | | total | 827.4 | | total | 6.65 |

**Table 2. Uranium, Plutonium concentrations and isotopic compositions in Zircaloy-4 hull**

| Uranium | | 1,132 mgU/kg-Zry | Plutonium | | 13.6mgPu/kg-Zry |
|---|---|---|---|---|---|
| Uranium Isotopes | U-234 | 0.025 wt% | Plutonium Isotopes | Pu-238 | 1.33 wt% |
| | U-235 | 1.19 wt% | | Pu-239 | 61.01 wt% |
| | U-236 | 0.38 wt% | | Pu-240 | 23.12 wt% |
| | U-238 | 98.41 wt% | | Pu-241 | 10.08 wt% |
| | - | - | | Pu-242 | 4.46 wt% |
| | total | 100wt% | | total | 100 wt% |

**Table 3. Radioactivity of hull calculated by ORIGEN-II code**

**(Ci/ton-Zry)**

| ASSY | DISCHARGE | 5.0YR | 10.0YR | 15.0YR | 20.0YR | 25.0YR | 30.0YR | 35.0YR | 40.0YR | 45.0YR | 50.0YR |
|---|---|---|---|---|---|---|---|---|---|---|---|
| U | 1.49E+00 | 2.16E-07 | 1.79E-07 | 1.50E-07 | 1.28E-07 | 1.11E-07 | 9.73E-08 | 8.69E-08 | 7.89E-08 | 7.28E-08 | 6.81E-08 |
| NP | 1.48E+00 | 1.50E-06 | 1.50E-06 | 1.50E-06 | 1.50E-06 | 1.50E-06 | 1.50E-06 | 1.50E-06 | 1.50E-06 | 1.50E-06 | 1.50E-06 |
| PU | 3.98E-02 | 7.33E-03 | 5.78E-03 | 4.57E-03 | 3.62E-03 | 2.86E-03 | 2.27E-03 | 1.81E-03 | 1.44E-03 | 1.16E-03 | 9.28E-04 |
| AM | 1.58E-02 | 7.76E-05 | 1.28E-04 | 1.67E-04 | 1.97E-04 | 2.21E-04 | 2.38E-04 | 2.52E-04 | 2.62E-04 | 2.69E-04 | 2.74E-04 |
| CM | 3.49E-03 | 1.48E-04 | 1.21E-04 | 1.00E-04 | 8.29E-05 | 6.87E-05 | 5.69E-05 | 4.71E-05 | 3.91E-05 | 3.24E-05 | 2.69E-05 |
| BK | 2.54E-10 | 1.08E-12 | 2.07E-14 | 3.97E-16 | 7.61E-18 | 1.30E-19 | 2.13E-22 | 2.13E-22 | 2.13E-22 | 2.13E-22 | 2.13E-22 |
| CF | 1.68E-12 | 9.83E-13 | 6.85E-13 | 5.32E-13 | 4.35E-13 | 3.67E-13 | 3.15E-13 | 2.76E-13 | 2.45E-13 | 2.21E-13 | 2.03E-13 |
| SUM(ci) | 3.03E+00 | 7.55E-03 | 6.03E-03 | 4.84E-03 | 3.90E-03 | 3.15E-03 | 2.57E-03 | 2.11E-03 | 1.75E-03 | 1.46E-03 | 1.23E-03 |
| Weight(g) | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 | 3.18E+05 |
| Ci/ton | 9.53E+00 | 2.37E-02 | 1.89E-02 | 1.52E-02 | 1.22E-02 | 9.91E-03 | 8.07E-03 | 6.63E-03 | 5.48E-03 | 4.58E-03 | 3.87E-03 |

**Table 4. Heat generation of hull calculated by ORIGEN-II code(W/kg-Zry)**

| ASSY | DISCHARGE | 5.0YR | 10.0YR | 15.0YR | 20.0YR | 25.0YR | 30.0YR | 35.0YR | 40.0YR | 45.0YR | 50.0YR |
|---|---|---|---|---|---|---|---|---|---|---|---|
| APWACHF | 8.16268 | 0.01946 | 0.00849 | 0.00948 | 0.00924 | 0.00864 | 0.00491 | 0.00253 | 0.00132 | 6.9E-05 | 3.7E-05 |

**Fig. 1. Oxygen potential on the inside of a Zircaloy hull.**

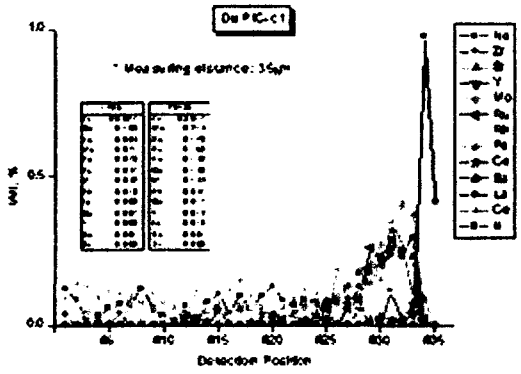

Fig.2. EPMA results of the inside of a Zircaloy hull

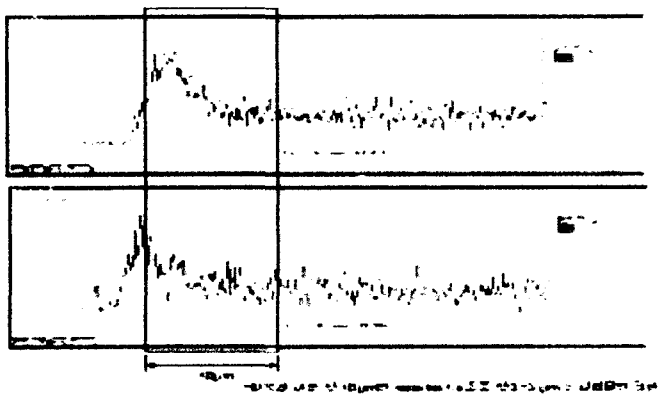

Fig. 3. Peeling-off of a Zircaloy hull by Laser