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# Investigation of PWR Hull with a View to Downgrade

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**Abstract:** The cladding materials remaining after the reprocessing of nuclear fuel, generally called hulls, are classified as high-level radioactive waste. They are usually packaged in a container for disposal after being compacted, melted, or solidified into a heterogeneous matrix. Efforts to fabricate a better waste form from an environmental perspective have failed due to the technical difficulties encountered in the chemical decontamination of cladding hulls. In the early 1990's, the accumulation of radiochemical data on hulls and the advent of new technology such as laser or plasma have made the decontamination of hulls a viable option.

This paper summarizes information regarding the radiochemical analysis of spent nuclear fuel hulls through a literature survey, including the characteristics of the hulls of 32,000 MWd/tU burn-up and 15 years cooling of Korean pressurized water reactor. The reduction of the radioactivity by peeling off the inner surface of the hulls via laser technology was evaluated.

**Keywords:** DUPIC, PWR, hull, characterization, peel off, dry process, decontamination

## INTRODUCTION

Spent PWR (Pressurized Water Reactor) nuclear fuels are typically stored at nuclear power plants until they are reprocessed or otherwise disposed. During the reprocessing of spent PWR fuel, the fuel rods are chopped into pieces about 3–5 cm long. The chopped fuel segments are dissolved in boiling nitric acid. The dissolved uranium and plutonium are reclaimed by separation and purification processes. This is aqueous reprocessing of nuclear fuel (1).

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Alternatively, the spent PWR fuel rods can be cut into 5 cm lengths for a DUPIC (Direct Use of Spent PWR Fuel in CANDU reactors) fuel fabrication process (2). The uranium powder is separated from the cladding materials through an OREOX (Oxidation and Reduction of OXide fuel) process (2). The basic concept of the DUPIC fuel cycle is to directly fabricate the CANDU (CANada Deuterium Uranium) fuel from spent PWR fuel by using thermal/mechanical processes at hot cells without separation of fission products and transuranic elements. OREOX process is a powdering step from a spent PWR fuel rod by repeating oxidation and reduction, resulting in $\sim 10\,\mu$ micron size particles separated from clad. The OREOX process is normally repeated 3 times at 450°C in air for oxidation and at 650°C in $H_2Ar$ for reduction (2).

The cladding materials remaining after the reprocessing of nuclear fuels are generally called hulls. Because the hulls are contaminated with fission products, activation products, and transuranic (TRU) radionuclides, they are categorized as a high-level radioactive or TRU waste.



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

The hulls, which constitute a quarter of spent nuclear fuel assembly by mass, are usually packaged in a container for disposal after being compacted, melted, or solidified into a heterogeneous matrix. Their ultimate disposal may be complicated by the presence of fission products, activation products and long-lived $\alpha$-emitting transuranic nuclides. Removing the long-lived transuranic nuclides from cladding hulls reduces the volume of TRU waste that requires special handling and treatment, and thereby, reducing the disposal cost (3). The efforts to fabricate a better waste form for hulls have failed due to technical difficulties encountered in the chemical decontamination of the hulls. In the early 1990s, the accumulation of radiochemical data on hulls and advances in technology development have made decontamination of the hulls more practical.

This paper summarizes information regarding the radiochemical analysis of spent nuclear fuel hulls through a literature survey, including the characteristics of the hulls of 32,000 MWd/tU burn-up and 15 years cooling of Korean pressurized water reactor. The reduction of the radioactivity by peeling off the inner surface of the hull via laser technology was evaluated.

## RADIOCHEMICAL CHARACTERISTICS OF HULLS FROM THE AQUEOUS REPROCESSING PROCESS

### Dose Rate and Radioactivity

Restani et al. (4) characterized the hulls originated from aqueous reprocessing of spent PWR fuel with a 30,000 MWd/tU burn-up and 5 years cooling. The fission

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

| Fission products | | Activation products | | $\alpha$–Nuclides | |
|---|---|---|---|---|---|
| Nuclide | Radioactivity (mCi/kg-Zry) | Nuclide | Radioactivity (mCi/kg-Zry) | Nuclide | Radioactivity (mCi/kg-Zry) |
| Cs-137 | 542 | Sb-125 | 760 | Pu | 4.51 |
| Ru-106 | 458 | Co-60 | 64 | Cm-244 | 1.24 |
| Cs-134 | 162 | Mn-54 | 3.4 | Am-24 I | 0.90 |
| Ce-144 | 70 | | | | |
| Eu-154 | 21 | | | | |
| Total | 1253 | Total | 827.4 | Total | 6.65 |



products, activation products, and $\alpha$-emitting transuranic nuclides remaining on the hull surface are shown in Table 1. Distribution patterns of fission products such as Cs-137, Sr-88, Ba-138, La-139, Eu-154 were reported within a 10 to 15 μm thickness from the hull surface. A total of 99.5% of the $\alpha$-nuclides such as Pu and U were distributed within 5 μm from the hull surface and decreased significantly from 5 to 15 μm. The other 0.5% of the $\alpha$-nuclides existed within a hull deeper than 20 μm. The $\gamma$ radioactivities for the hulls were measured with a high purity Ge detector. The $\gamma$ dose rate at a distance of 0.5 m ranged 10–50 mR/hr (average $25 \pm 8$ mR/hr). The species of the fission products were identified from the analysis of the gamma ray spectrum obtained by gamma spectrometry. The $\beta$ and $\gamma$ radioactivity from the hulls were dominated by Sb-125 from the alloying element tin.

## Actinide Analysis of Zircalloy Hulls

A specimen of the zircalloy-4 hull was dissolved in 3 *M* $HNO_3$/2 *M* HF. The actinide content was obtained by the isotope dilution analysis method. The results are shown in Table 2. Table 2 shows that the average content of uranium and plutonium are 1,132 mgU/kg-Zry (Zry: zircalloy) and 13.6 mgPu/kg-Zry, respectively. In addition, the result of the $\alpha$-autoradiography to evaluate the qualitative TRU distribution showed that the contents of uranium and plutonium ranged 380–2,130 mgU/kg-Zry and 6.3–25.3 mgPu/kg-Zry, respectively.

## SIMS Analysis of Zircalloy Hulls

The concentration depth profile of the radionuclides was analyzed with a shielded secondary ion mass spectrometer (SIMS) by Restani (4). The

*Table 2.* Average uranium and plutonium concentrations and isotopic compositions in Zircalloy-4 hull (4)

| Uranium | 1,132 mgU/kg-Zry | Plutonium | 13.6 mgPu/kg-Zry |
|---|---|---|---|
| Uranium Isotopes | | Plutonium isotopes | |
| U-234 | 0.025 wt% | 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-24 I | 10.08 wt% |
| | | Pu-242 | 4.46 wt% |
| Total | 100 wt% | Total | 100 wt% |



SIMS analysis showed that uranium adhered mainly to the inner surface of zircalloy tube and that the concentration in the oxide layer dropped sharply. Fission products penetrated at a considerable distance to about 10 μm as recoil particles. The smallest element, Sr-88, penetrated the farthest distance of 12 μm. It was also reported that the outside oxygen layer of the hull surface ranged 6–12 μm while the inside was 1–2 μm for the hull generated from the aqueous reprocessing.

## RADIOCHEMICAL CHARACTERISTICS OF THE HULLS FROM THE DUPIC FUEL FABRICATION PROCESS

### Hulls from the DUPIC Fuel Fabrication Process

DUPIC fuel fabrication consists of decladding, powder preparation, pelletizing, and fuel element manufacturing processes. The sample hulls are chosen from a DUPIC fuel fabrication process using spent PWR fuel rods with a 32,000 MWd/tU burn-up and 15 year cooling time.

### Oxide Layer

The oxide layer that 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 an outside layer forms due to the reaction with the reactor coolant. The thickness of the outside oxide layer is thicker than that of the one inside. Sometimes, $\alpha$-nuclides such as Pu and U may be embedded inside the oxide layer due to the collision with heavy fission fragments.

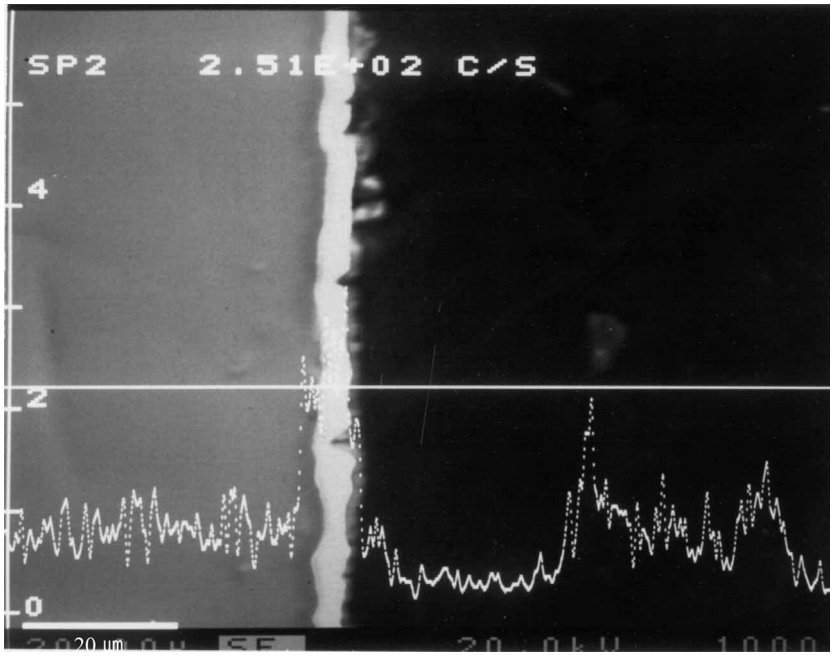


***Figure 1.*** Oxygen intensity at the inner surface of zircalloy hull of 32,000 MWd/tU burn-up (right is fuel side).

Thickness of oxide layer at inner surface of the hull was about 3 μm as shown in Fig. 1. The intensity was measured using EPMA (Electron Probe Microscope Analyzer) and the bright gray colored bar at Fig. 1 represents the oxide layer on the hull.

Figure 2 shows two overlapped pictures of plutonium and oxygen intensities measured by EPMA. The upper graph is for plutonium and lower one is for oxygen. The left is the nuclear fuel side. The beginning point of measurement of both graphs was coincident with each other. It shows that the amount of $\alpha$-nuclides at the hull surface decreases dramatically. And also, it shows that fission products, especially zirconium, exist in oxide forms, because the oxygen concentration increases to the depth of 3 μm from the maximum peak of plutonium.

## EPMA Analysis of the Inside Surface of the Hull

A 1 cm long sample for EPMA was prepared by cutting and mounting a hull. The results of the EPMA analysis for 35 detection points with 1 μm distance are shown in Fig. 3. It was found that most of the radionuclides are distributed within a thickness of 10 μm (between #25–#35). Zr was the major element

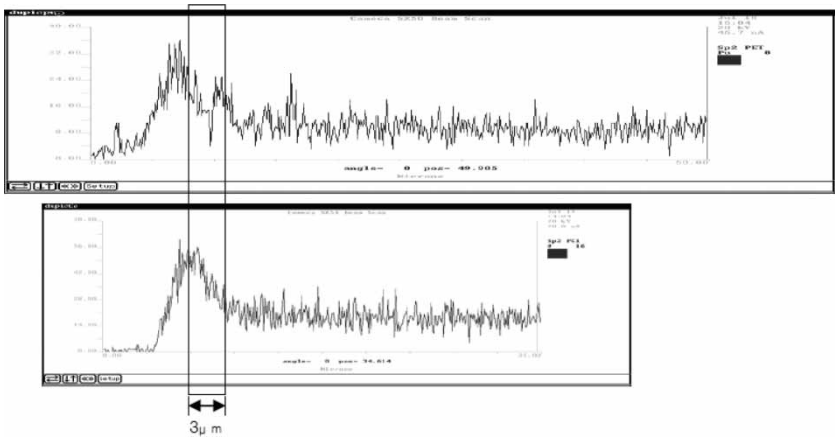


***Figure 2.*** Plutonium and oxygen intensities at the inner surface of zircalloy hull of 32,000 MWd/tU burn-up.



with a composition equal to 98.9%, while the other fission product elements make up the balance.

The radiochemical characteristics of the hull from DUPIC process was similar to that of Restani et al.

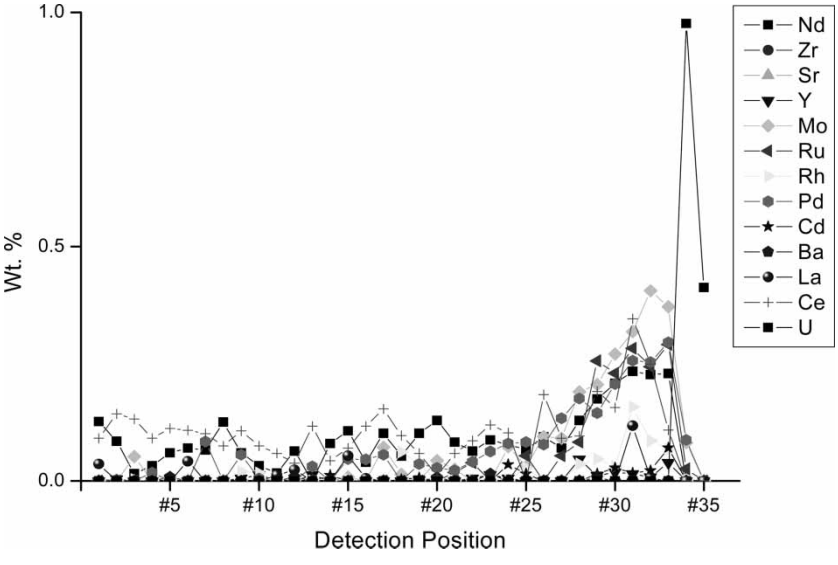


***Figure 3.*** Concentration profile of fission products by EPMA at inner surface of a zircalloy hull of 32,000 MWd/tU burn-up (right is fuel side).

***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 |
|---|---|---|---|---|---|---|---|
| U | 1.49E + 00 | 2.16E-07 | 1.79E-07 | 1.50E-07 | 1.28E-07 | 1.11E-07 | 9.73E-08 |
| NP | 1.48E + 00 | 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 |
| AM | 1.58E-02 | 7.76E-05 | 1.28E-04 | 1.67E-04 | 1.97E-04 | 2.21E-04 | 2.38E-04 |
| CM | 3.49E-03 | 1.48E-04 | 1.21E-04 | 1.00E-04 | 8.29E-05 | 6.87E-05 | 5.69E-05 |
| BK | 2.54E-10 | 1.08E-12 | 2.07E-14 | 3.97E-16 | 7.61E-18 | 1.30E-19 | 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 |
| SUM(Ci) | 3.03E + 00 | 7.55E-03 | 6.03E-03 | 4.84E-03 | 3.90E-03 | 3.15E-03 | 2.57E-03 |

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

| ASSY | AP + ACT + FP |
|---|---|
| Discharge | 8.162688 |
| 5.0YR | 0.019246 |
| 10.0YR | 0.008439 |
| 15.0YR | 0.003948 |
| 20.0YR | 0.001924 |
| 25.0YR | 0.000964 |
| 30.0YR | 0.000491 |



## FEASIBILITY OF RADIOACTIVITY REDUCTION BY PEELING OFF THE INNER HULL SURFACE

### Inherent Radioactivity Arising from Potential U Impurity in Zircalloy-4

Transuranic nuclides may arise from U impurities that are distributed uniformly throughout the zircalloy tube. The radioactivities due to these transuranic nuclides are calculated using the ORIGEN-II code and the results are shown in Table 3. Calculation was carried out for 35,000 MWd/tU burn-up according to cooling time. It shows that the zircalloy cladding tube potentially containing up to 3.5 ppm of uranium as impurity in the cladding leads to a 0.00755 Ci/ton-Zry (7.55 nCi/g-Zry) radioactivity rise at 5 years from discharge, which is less than the TRU criterion of 100 nCi/g. Therefore, in this case hulls would not be categorized as a TRU waste solely by the transuranic nuclides arising from potential U impurities. This indicates that the hulls may be converted to non-TRU waste by removing other actinides that exist in the hull surface by peeling-off the inner hull surface.

### Radioactivity Reduction

From the results of characterizing hulls as above, peeling off the inner hull surface by 20 μm can reduce the total activity of hull due to the elimination of the fission products and $\alpha$-nuclides from radioactivity perspective. The removed surface would be classified as TRU waste and this equivalents to about 3% comparing to the whole thickness of 760 μm.

***Table 5.*** Waste classification by 10CFR61.55 Table 1(ORIGEN-II calculation basis of cladding hull: Burn-up = 35,000 MWd/tU, Power rate = 37.5 MW/tU, 5 yrs cooling)

| 10 CFR 61.55 Waste Classification in Table 1 | | | | |
|---|---|---|---|---|
| Radionuclide | Concentration curies per cubic meter | ORIGEN-II Code PWR cladding hull after 10yrs Cooling | Fraction By 10CFR 61.55(a)(3)(ii) (iV) | Remark |
| C-14 | 8 | 9.36E−11 | 1.17E−11 | |
| C-14 in activated metal | 80 | 1.04E + 01 | 1.30E−01 | |
| Ni-59 in activated metal | 220 | 5.64E−02 | 2.56E−04 | |
| Nb-94 in activated metal | 0.2 | 1.48E−07 | 7.40E−07 | |
| Tc-99 | 3 | 2.07E−04 | 6.90E−05 | |
| I-129 | 0.08 | 3.14E−08 | 3.93E−07 | |
| SUM | 311.28 | 1.05E + 01 | 1.30E-01 | 0.13 |
| Alpha emitting transuranic nuclides with half-life greater than 5 years | 100 | 1.35E + 00 | 1.35E-02 | *a* |
| Pu-241 | 3,500 | 1.83E + 01 | 5.23E−03 | *a* |
| Cm-242 | 20,000 | 2.79E−03 | 1.40E−07 | *a* |
| SUM | 23,600 | 1.97E + 01 | 1.87E−02 | 0.02 |

[a]Units are nanocuries per gram.

***Table 6.*** Waste classification by 10CFR61.55 Table 2 (ORlGEN-II calculation basis of cladding hull: Burn-up = 35,000 MWd/tU, Power rate = 37.5 MW/tU, 5 yrs cooling)

| 10 CFR 61.55 Waste classification in Table 2 | | | | | | |
|---|---|---|---|---|---|---|
| | Concentration curies per cubic meter | | | ORIGEN-II Code PWR cladding hull after 10 yrs cooling | Fraction By 10CFR 61.55(a)(5)(ii) | |
| Radionuclide | Col. 1 | Col. 2 | Col. 3 | | | Remark |
| Total of all nuclides less than 5 year half-life | 7.00E + 02 | *a* | *a* | — | | |
| H-3 | 4.00E+01 | *a* | *a* | — | | |
| Co-60 | 7.00E+02 | *a* | *a* | — | | |
| Ni-63 | 3.50E+00 | 7.00E + 01 | 7.00E + 02 | — | | |
| Ni-63 in activation product | 3.50E+01 | 7.00E + 02 | 7.00E + 03 | 3.16E + 01 | 4.51E−03 | |
| Sr-90 | 4.00E−02 | 1.50E + 02 | 7.00E + 03 | 6.64E−01 | 9.49E−05 | |
| Cs-137 | 1.00E + 00 | 4.40E + 01 | 4.60E + 03 | 1.27E + 00 | 2.75E−04 | |
| SUM | | | 1.93E + 04 | 3.35E + 01 | 4.88E−03 | 0.005 |

[a]There are no limits established for these radionuclides in Class B or C wastes.

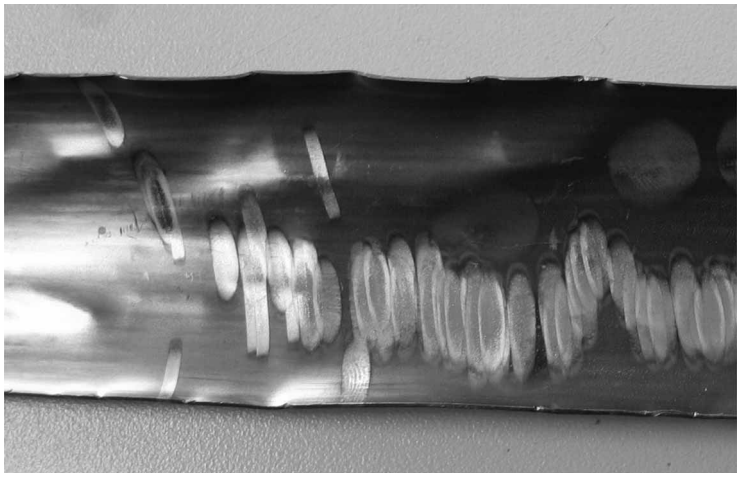

*Figure 4.* Peeled-off surface of a zircalloy hull by laser.



## Heat Generation from the Hull

The TRU waste criteria include a heat generation limit of $2\,kW/m^3$. Heat generation of $2\,kW/m^3$ is equal to about $0.31\,W/kg$, assuming a theoretical ingot density. The thermal characteristic of the hull is calculated using the ORIGEN-II code and the result is shown in Table 4. Table 4 shows the heat generation will naturally fall down to $0.0192\,W/kg$ at 5 years from

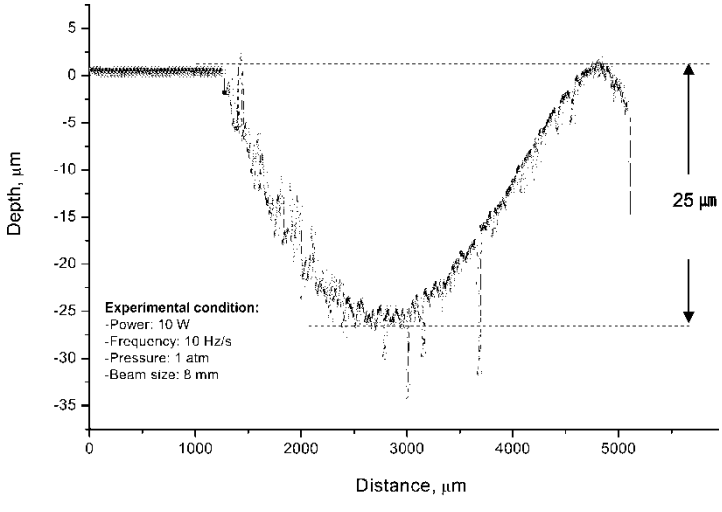


*Figure 5.* Peeled-off depth by a shot of laser.

discharge, which is far below the TRU waste criterion of 0.31 W/kg. No additional effort is needed to reduce the heat generation below the TRU waste criterion because the heat generation drops below 1/600 of this value after the average storage period of 30 years.

## Waste Classification by 10CFR61.55

Tables 5 and 6 show the activity of peeled-off PWR cladding hull after 10 years cooling calculated using the ORIGEN-II code versus criteria from 10CFR61.55 waste classifications (5). 10CFR61.55 Waste classification (a) (5) (ii) says that "If the concentration of a nuclide listed in Table 5 exceeds 0.1 times the value listed in Table 5 but does not exceed the value in Table 5, the waste shall be Class C, provided the concentration of nuclides listed in Table 6 does not exceed the value shown in Column 3 of Table 6."

According to the sum of fractions rule described in 10CFR61.55, the sum of fractions of peeled-off cladding hull is 0.15 which is less than 1.0 and also does not exceed Column 3 of Table 6; therefore, the peeled-off cladding hull can be classified as "Class C" waste.

## Peeling off a Zircalloy-4 Cladding Hull

The inner surface of a non-radioactive zircalloy-4 cladding hull was peeled-off by applying a laser technique. The result is shown in Figs. 4 and 5. The depth of a laser shot on the surface of the hull was 25 μm. A laser shot was made 10 W power, 10 Hz/s frequency and 8 mm beam size at 1 atm. Contours in Fig. 5 were measured by Hommel Tester T8000 wavesystem™ (Germany). It is quite feasible to peel off the inner hull surface as much as is needed.

## CONCLUSIONS

With about a 20 μm peeling-off of the inner surface of hull, the total radioactivity from the hull surface after 5 years cooling would reduce to 7.55 nCi/g of Zry, which is below the TRU waste criterion of 100 nCi/g of Zry. After 5 years from discharge, the heat generation from the hull would drop to 0.0192 W/kg which is well below the TRU waste criterion of 0.31 W/kg. The 20 μm peeling-off of the inner 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 "Class C" waste by a 20 μm removal of the inner surface of hull after 10 years cooling.

## ACKNOWLEDGMENT

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