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# Review of Destructive Assay Methods for Nuclear Materials Characterization from the Three Mile Island (TMI) Fuel Debris

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# ACKNOWLEDGEMENT

The author wishes to acknowledge the research performed by prior research teams at Idaho National Laboratory that focused on studying the Three Mile Island 2 nuclear power plant reactor accident including accident scenarios, reactor and fuel cleanup, fuel storage, and decontamination and cleanup principles. I would specifically like to acknowledge Dr. Doug Akers for the work that he performed in characterizing the molten fuel and containment debris and providing destructive analysis measurements for post-accident nuclear material accountancy.

# EXECUTIVE SUMMARY

This report provides a summary of literature reviewed discussing previous work performed at the Idaho National Laboratory studying the Three Mile Island 2 (TMI-2) nuclear reactor accident and focusses specifically on the melted fuel debris containing the majority of the fuel materials. The purpose of the literature review was to document prior published work that supports the feasibility of the analytical techniques that were developed to provide quantitative results of the make-up of the fuel and reactor component debris located inside and outside the containment. The quantitative analysis provides a technique to perform nuclear fuel accountancy measurements.

Debris for dissolution eas expected to have formed at high temperatures and contain silicates and other hard-to-dissolve materials. The debris was typically in a glassy matrix containing plutonium and uranium with radioactive fission products. The report 1) summarizes the TMI debris characteristics at various locations in the reactor system, 2) assesses the preprocessing and dissolution methods for destructive assay of the various types of debris, 3) describes the radiochemical debris destructive measurement methods, and 4) assesses the calibration and error estimation for measurements using destructive assay.

TMI-2 samples were dissolved using a pyrosulfate fusion technique in a closed system. Iodine-129 tracer was added to the intact sample before dissolution, and Sr-90 was added after dissolution. This technique was used to allow measurement of the I-129 content of the sample. Corium samples that were larger in size were processed through several steps including: grinding to get samples 5-10 mg up to a gram maximum, a sequential dissolution beginning with nitric acid, then followed by hydrofluoric acid. Some samples were leached using a potassium permanganate solution and sometimes a sodium or ammonium (alkaline) permanganate solution was used. The most important step in all the analytical processes was the pyrosulfate fusion to obtain the uranium amounts**.** Nitric acid was used to oxidize metals and alloys to soluble nitrates and the hydrofluoric acid was used to get rid of any silicates and dissolve the oxides of Nb, Ta, Ti and Zr. Standard pyrosulfate fusions were used for nuclear accountability.

This report is intended to provide knowledge obtained throughout the sampling, fuel storage, and cleanup processes at the TMI-2 nuclear reactor accident site as a path forward for nuclear material accountancy measurements necessary for the Fukushima Daiichi nuclear power plant in Japan. Lessons learned from the TMI-2 nuclear reactor accident may be applicable to the cleanup and nuclear material accountancy of the destroyed Fukushima Daiichi nuclear reactor.

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# 1. INTRODUCTION

This report provides a summary of the literature review that was performed and based on previous work performed at the Idaho National Laboratory studying the Three Mile Island 2 (TMI-2) nuclear reactor accident, specifically the melted fuel debris. The purpose of the literature review was to document prior published work that supports the feasibility of the analytical techniques that were developed to provide quantitative results of the make-up of the fuel and reactor component debris located inside and outside the containment. The quantitative analysis provides a technique to perform nuclear fuel accountancy measurements.

The author has directly quoted many parts of this document; however, to make it more readable the direct quotations have been omitted.

# 2. BACKGROUND

Unit 2 of the Three Mile Island pressurized water reactor (PWR) underwent a loss of coolant accident on March 28, 1979 which resulted in severe damage to the reactor core. Samples of the lower core were taken to spatially characterize the chemical and physical state of the degraded core. Nondestructive (visual examination, photography, sample weight, bulk sample density, and individual particle density) and destructive examinations (optical metallography, scanning electron microscopy (SEM), and radiochemical analysis) provided data of fission product release, interaction between core components, hydrogen generation, and core melt progression. The TMI debris characteristics at various locations in the reactor system may be useful to describe similar events. In addition, following the detonation of a nuclear device, solid debris samples are expected to contain trace-level quantities of nuclear materials combined with material from the immediate environment around the detonation site, which may have been activated and is assumed to have been vaporized and re-condensed. As such, debris for dissolution is expected to have formed at high temperatures and contain silicates and other hard-to-dissolve materials. Solid fallout debris is typically in a glassy matrix containing parts per million (ppm) quantities of plutonium or uranium with radioactive fission products. The following report 1) summarizes the TMI debris characteristics at various locations in the reactor system, 2) assesses the preprocessing and dissolution methods for destructive assay of the various types of debris, 3) describes the radiochemical debris destructive measurement methods, and 4) assesses the calibration and error estimation for measurements using destructive assay.

## 2.1 CHARACTERIZATION OF FUEL DEBRIS FROM THE LOWER HEAD OF THE REACTOR VESSEL

Fuel debris samples were taken from near the lower head of the reactor vessel [1]. Two types of samples were obtained: (1) nozzle and guide tube samples from the vessel and the flow distributor and (2) fuel solidified debris samples removed from the surface of the lower head [1, 2]. The debris samples ranged from <5 cm to 45 cm in the central part of the lower head. Outside of this region the solidified debris was ~26 cm. The debris samples were taken from within 30 cm of the lower head generally but the ones near the periphery of the molten pool were taken within 15 cm [1]. Metallography was performed on the debris samples and results showed that the debris samples consisted primarily of previously molten $(U,Zr)O_2$ with pores formed in stratified layers surrounded by microporosity and two phase structures $(U,Zr)O_2$ and $(Zr,U)O_2$ [1]. The microstructure is indicative of a solidified $(U,Zr)O_2$ ceramic melt, rich in uranium. The presence of two phases indicates that the samples were not rapidly quenched but underwent a

gradual cool down and that the single phase regions solidified first [1]. Debris samples were fully oxidized which suggests the presence of sufficient steam to oxidize all available zirconium [1]. The debris bed appears to be homogeneous based on the bulk elemental composition and is composed primarily of fuel element components with relatively small amounts of structural components. Elemental analysis results indicates the composition of the debris bed to be 70 wt% U, 13.75 wt% Zr, and 13 wt% O, and 3 wt% elemental constituents of the stainless steel and inconel core components [1]. Striation or interconnected porosity seen in many of the samples may be due to bubbling of steam or structural material vapors through the molten pool. These samples show that the debris was liquid while on the lower head and remained liquid for sufficient time to allow bubble formation [1].

Scanning electron microscopy (SEM) analysis was also performed on debris bed samples. The SEM analysis was used to determine the core constituents, primarily U, O, Zr, Ag, Al, Cd, Cr, Fe, In, Mg, Mo, Mn, Nb, Ni, Sn, and some fission products. The samples were examined around the edge of large pores, metallic inclusions, secondary phases, and pores without secondary phases. The homogeneous $(U,Zr)O_2$ matrix had relatively low concentrations of Al, Mg, Sb, and Sn. There was a zirconium-rich secondary phase around the pores and at grain boundaries. There also was the presence of oxidized Fe and Cr inclusions which suggests the remains of nozzle and other vessel components that were melted during the relocation of the fuel. [1] Metallic inclusion samples are composed primarily of metallic silver with trace amounts of Zr and other metals. The other control rod constituents (In and Cd) wer not present which suggests that the control rod material had been heated sufficiently to volatilize the In and Cd from the Ag [1]. Secondary phases around pores and in the debris matrix indicates the secondary phases are primarily $(Zr,U)O_2$ with greater amounts of Fe and Cr present. The presence of the localized Fe and Cr suggests that there was not a great deal of mixing after the material was deposited on the lower head [1].
Radiochemical analysis was performed to assess bulk composition and radionuclide content. Prior to destructive radiochemical analysis, intact samples were analyzed by gamma spectroscopy to provide an estimate of the gamma-emitting radionuclide content. The samples were then dissolved and elemental analysis was performed using inductively coupled plasma (ICP) spectroscopy techniques. The results appear in Table 1 [1]. From the table, it appears that the fuel melt is composed almost entirely of the constituents of the fuel rod and there are little structural constituents.

Table 1: Elemental analysis results of Debris Adjacent to the Lower Head of the TMI-2 Reactor Vessel

| **Element** | **Average Core Composition TMI-2 (if core was homogeneously mixed including end fittings) (wt. %)** | **Average Debris Composition (wt. %)** |
|---|---|---|
| U | 65.8 | 70.4 |
| Zr | 18.0 | 13.8 |
| O | 8.5 | Cannot be measured with this technique |
| Fe | 3.0 | 0.73 |
| Ag | 1.8 | Not detected (some may have been lost during analysis due to method used) |
| Cr | 1.0 | 0.37 |
| Ni | 0.9 | 0.09 |
| In | 0.3 | 0.27 |
| Sn | 0.3 | Not detected |
| Al | 0.2 | Not detected |

| | | |
|---|---|---|
| B | 0.1 | Not reported |
| Cd | 0.1 | Not reported |
| Mn | 0.8 | 0.028 |
| Nb | 0.04 | Not detected |
| Total | 100.84 | --------- |
| Total minus O | 92.34* | 85.69* |
| *Difference in core composition and debris composition can be accounted for by the oxidation of the uranium and zirconium in the samples | | |

Radiochemical analysis of the debris samples indicate that the volatile radionuclides (noble gases, cesium and iodine) had volatilized from the bed with only the medium and low-volatile radionuclide remaining [1]. High volatility fission products are the noble gases, halogens, alkali metals, and heavy chalcogens. Only measurements of I-129 and Cs-137 were made. The medium volatility fission products are the alkaline earth metals, some of the rare earth metals, and actinides. Radionuclides from this group are Sb-125, Sr-90, Eu-154, and Ru-106. The low-volatility fission products are the noble metals, the remaining rare earth metals, tetravalents, and early transition elements. The only radionuclide from this group that was measurable was cerium/praseodymium. Table 2 contains information from the radionuclide analysis of the debris bed.

Table 2: Radionuclide analysis results of Debris Adjacent to the Lower Head of the TMI-2 Reactor Vessel

| Radionuclide | ORIGEN2 Code Adjusted Radionuclide Concentration* Microcuries/g U | Debris Bed % composition based on Uranium analysis | Debris Bed Radionuclide Concentration Microcuries/g U |
|---|---|---|---|
| | | | |
| Sr-90 | 8330 | 64 | 5331 |
| Ru-106 | 413 | - | - |
| Sb-125 | 308 | 2.9 | 8.9 |
| I-129 | 0.003 | - | - |
| Cs-137 | 9680 | 7.6 | 735.7 |
| Ce-144 | 617 | 91 | 561.5 |
| Eu-154 | 80 | 82 | 65.6 |

*Correction to the core average value to account for the fact that the peripheral 2.98% enriched fuel assemblies did not participate in the accident.

## 2.2 CORE BORE SAMPLES BELOW THE DEBRIS BED IN THE LOWER REACTOR REGION

Core bores were taken from the region below the debris bed in the lower reactor core region. Physical, metallurgical, and radiochemical measurements were performed. The upper reactor core contained a void region. Below the void region was a layer of debris resting on a hard crust with approximately 50% of the core volume located below the debris bed [3]. The core below the debris bed had a region of previously molten material surrounded by a hard crust and a second region of intact standing fuel rods extending from the bottom of the previously molten region to the bottom of the core.

The core bores contained solid plugs of the upper and lower crusts, previously molten material from between the crusts, and fuel rod stubs. Solid plugs from the upper and lower crusts were composed of agglomerated fuel and structural material components. The upper crust and the lower crust had different compositions from each other. The upper crust was a mixture of debris agglomerated with metallic material. The lower crust consisted of fuel rods surrounded by solidified molten material. The region between the crusts was relatively homogenous with longer fuel rod stubs located near the periphery and shorter fuel rod stubs located near the core [3].

Gamma spectroscopy was performed on the core bores followed by isotopic analysis at 2.5cm intervals over the length of the bore and at areas of high activity identified during gamma radiation measurements [3]. Upper and lower crust regions had significant concentrations of Co-60, Ru-106, and Sb-125. The molten material between the crust layers has low concentrations of volatile radionuclides such as Co-60, Ru-106, and Sb-125. The molten material between the crusts has low concentrations of volatile radionuclides but has significant amounts of Ce-144 and Eu-154. The fuel rod sections in the lower core have high concentrations of high volatile fission products [3].

Metallurgical examinations of the molten material found in the coolant channels of the lower crust area was a mixture of metallic structural and control rod components. Two metallic phases were present with the main constituents of: 1) Zr, Fe, Ni, Cr and 2) Ag, In alloy. Some cadmium from the control rods was present in the Ag phase [3].

Samples from the lower vessel plug suggest an interaction between the fuel rods and the structural components which resulted in the dissolution of the zircaloy cladding and fuel by the molten structural materials. Fission products in the lower crust were retained in the fuel material [3].

The upper crust plugs had two phases: 1) ceramic phase containing mostly fuel material components and 2) metallic phase of mostly structural components. The ceramic phase is an interaction of fuel rods and structural/control rod components and is more concentrated in the lower crust region. There are no intact fuel rods in the ceramic phase and the structural materials are present as oxides of nickel, silver, and indium. The ceramic phase also contains uranium and zirconium oxides with small amounts of iron, chromium and nickel [3**].** Intact fuel pellet remnants were encased intact in the ceramic matrix with the mixed oxides of uranium and zirconium. **The ceramic phase is the phase where it is important to be able to do nuclear material accountancy.**

The peripheral crust is the region of the upper crust near the mid-radius of the core. This crust has substantial amounts of metallic structural components: iron, nickel, silver, and indium [3]. Samples from the core interior particles are a mixture of both metallic and ceramic phases. The metallic samples are dendritic and composed of iron, nickel, and chromium with circular inclusions of silver, indium and tin. Some contained spherical particles of chromium oxide. The most common fission product in the metallic inclusions was ruthenium and technetium along with measurable concentrations of palladium and tellurium [3]. Fuel rods and guide tubes indicated hydriding. No previously molten debris was present between the intact fuel and control rods in the core bore [3].

Tables 3-5 summarize the core materials and fission product inventory from the TMI-2 reactor [4]. Table 3 is a summary of the post-accident core materials distribution, Table 4 is the fuel material and control rod distribution on the reactor vessel, and Table 5 is a summary of the fission

product results on the reactor vessel [4]. The low volatiles were not released from the fuel and only a small amount was transported to the reactor coolant system is intact or melted. These three low volatility fission product numbers can be used to calculate the plutonium and uranium concentrations for nuclear material inventories based on the ORIGEN2 code because they were not lost during the TMI-2 accident. The Ce-144 concentration is the most accurate because Ce-144 is produced by direct beta decay from fission of the UO2 while the Eu-154 and Eu-155 are produced by neutron activation of fission products and are dependent on the neutron flux and spectrum and on the core location of the fuel material. Therefore the Ce-144 concentration was used to calculate the nuclear material inventory for all samples sent to Idaho National Laboratory [4].

Table 3: Summary of post-accident core materials distribution (Estimated) [4]

| Core Region | Estimated quantity (kg) | Uncertainty[(a)] (%) | Percent of total core (%) |
|---|---|---|---|
| | | | |
| Intact fuel assemblies (partially or fully intact) | 44500 | 5 | 33.4 |
| Central core region resolidified mass | 32700 | 5 | 24.5 |
| Upper core debris bed | 26600 | 5 | 19.9 |
| Prior molten material on the lower reactor vessel head | 19100 | 20 | 14.3 |
| Lower core support assembly [(b)] | 5800 | 40 | 4.3 |
| Upper core support assembly[(b)] | 4200 | 40 | 3.2 |
| Outside the reactor vessel | 100 | (c) | 0.3 |

(a) The uncertainty estimates are based on defueling. Those areas that have been defueled have lower uncertainties.

(b) The lower core support assembly is the portion of the reactor vessel below the core that includes the lower grid assembly and five flow distributor plates. The upper core support assembly is a coolant flow region outside the vertical baffle plates that is the peripheral boundary of the core.

(c) Estimates of the amount of fuel material outside the reactor vessel are based on non-destructive evaluations of reactor components in the reactor and auxiliary buildings. They range from 60-100 kg.

Table 4: Fuel material and control rod materials distribution in the reactor vessel [4]

| Core material repositories | Core material distribution of fuel material [(a)] | | | Core material distribution of control rod materials [(a)] | | |
|---|---|---|---|---|---|---|
| | Uranium | Zirconium | Tin | Silver | Indium | Cadmium |
| Upper reactor plenum | (b) | (b) | (b) | 1.0 | (b) | (b) |
| Upper core debris | 24 | 13 | (c) | 1.8 | (c) | (c) |
| Upper crust region | | | | | | |
| • Ceramic | 1.3 | 1.2 | 2.3 | 1.2 | 3.6 | 0.65 |
| • Metallic | -- | 0.3 | 6.1 | 2.4 | 3.3 | 0.39 |
| Consolidated region | | | | | | |
| • Ceramic | 12 | 18 | -- | 10 | 27 | 6.1 |
| • Metallic | -- | 0.2 | 5.8 | 1.6 | 2.1 | 1.1 |
| Lower crust region | | | | | | |
| • Ceramic | 3.6 | 2.8 | 9.3 | 7.3 | 7.2 | 1.4 |
| • Metallic | -- | 5.6 | 26 | 11 | 16 | 2.9 |
| Intact fuel rods (d) | 33 | 33 | 33 | 11 | 11 | 11 |
| Lower reactor vessel head | 15 | 11 | (c) | (c) | (c) | (c) |
| Lower core support assembly | 4.6 | 3.3 | (c) | (c) | (c) | (c) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Upper core support assembly | 3.3 | 2.4 | (c) | (c) | (c) | (c) |
| | | | | | | |
| **TOTAL** | **97** | **91** | **82** | **47** | **70** | **23** |

(a) Percentage of the total amount of the element originally present in the core
(b) Insignificant amount (<0.1 wt%) based on the upper plenum measurements
(c) Elemental constituent not detected based on detection limits of approximately 0.1 wt%
(d) Only 70% of the partially intact fuel assemblies contain control material as the balance (22.7%) are peripheral assemblies which do not contain control materials

Table 5: Fission product distribution in the reactor system [4]

| **Fission Product Repositories** | **Fission product distribution Low volatility fission products Percent of inventory [a]** | | | **Fission product distribution Medium volatility fission products Percent of inventory [a]** | | | **Fission product distribution High volatility fission products Percent of inventory [a]** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Ce-144** | **Eu-154** | **Eu-155** | **Sr-90** | **Ru-106** | **Sb-125** | **Cs-137** | **I-129** | **Kr-85** |
| | | | | | | | | | |
| *Ex-vessl*<br>Containment atmosphere, basement, and tanks | 0.01 | (b) | (b) | 2.1 | 0.5 | 0.7 | (b)<br>47 | (b)<br>(47) [c] | 54<br>(b) |
| Reactor coolant system | (b) | (b) | (b) | 1 | (b) | 0.2 | 3 | 1 | (b) |
| Auxiliary building | (b) | (b) | (b) | 0.1 | (b) | 0.7 | 5 | 7 | (b) |
| | | | | | | | | | |
| *In-vessel* | | | | | | | | | |
| Upper reactor plenum | (b) | (b) | (b) | (b) | (b) | (b) | (b) | (b) | (b) |
| Upper core debris-A | 26 | 30 | 24 | 23 | 14 | 13 | 5.3 | 5.9 | 6 |
| Upper core debris-B [c] | 20 | 19 | 19 | 19 | 16 | 24 | 4.3 | 5.3 | (b) |
| Upper crust region<br>• Ceramic<br>• metallic | 1.4 | 2.0 | 1.6 | <br>0.73<br>(b) | <br>0.8<br>3.8 | <br>0.5<br>7.8 | 0.41 | 0.27 | (b) |
| Consolidated region<br>• ceramic<br>• metallic | 24 | 32 | 22 | <br>8.3<br>(b) | <br>2.2<br>9.0 | <br>3.1<br>6.9 | 0.77 | 2.1 | (b) |
| Lowe crust<br>• ceramic<br>• metallic | 5.9 | 7.9 | 5.1 | <br>4.5<br>(b) | <br>5.7<br>24 | <br>7.4<br>36 | 1.4 | 3.5 | (b) |
| Intact fuel rods | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Upper core support assembly | 3.4 | 4.5 | (d) | 3.9 | 0.23 | 0.22 | 0.46 | 0.12 | (b) |
| Lower core support assembly | 4.7 | 6.3 | (d) | 5.3 | 0.32 | 0.30 | 0.63 | 0.16 | (b) |
| Lower head-reactor vessel | 16 | 21 | (d) | 18 | 1.1 | 1.0 | 2.1 | 0.54 | (b) |
| | | | | | | | | | |
| **TOTAL** | **105** | **122** | **110 [d]** | **93** | **94** | **119** | **95** | **97** | **91** |

(a) Percentage of total amount of the fission product inventory calculated from comparisons with ORIGEN2
(b) Insignificant amount (<0.1 wt%) based on the upper plenum measurements
(c) Two sets of bulk sample measurements were performed on the upper debris bed. The A series was performed on 16 $cm^3$ sample from near the center of the core at a variety of depths whereas the B series were bulk samples from near the bottom of the debris bed. The data provide a range. For the totals, the B series data were used.
(d) Measurements not performed for this radionuclide at this core location. The total shown value in parenthesis is a total which assumes the same distribution as Eu-154 for the repositories where measurements were not performed

# 3. DESTRUCTIVE ASSAY TECHNIQUES

DA measurements provide a more accurate quantifiable measurement than non-destructive assay techniques and can be used to determine if a small fraction of a material is present. Destructive assay techniques are similar for all sample types. Common radiochemical techniques are: gravimetric methods spectrophotometric methods, electrometric titration methods (potentiometric, amperometric, and coulometric), fluorometry, x-ray fluorescence, x-ray absorption edge densitometry (K-edge), alpha spectrometric methods, and mass-spectrometric methods. The key to DA being quantitative and useful lies in the sample preparations. There are three main types of sample preparations for non-liquid samples: fusion, wet-ashing including acid leaching and acid dissolution, and microwave digestion. Brief descriptions of the techniques are provided in the following subsections [6].

Fusion and wet ashing are used to decompose most samples analyzed in radioanalytical laboratories. Fusion techniques are used for total dissolution of a difficult sample matrix. Leaching techniques are used to determine the soluble fraction of the radionuclide of interest. [6]

## 3.1 Gravimetric Analysis

Gravimetric methods involve separating a compound of an element and igniting it to a constant-weight stoichiometric compound. The technique is applicable to relatively pure materials such as $U_3O_8$, $UO_2$, or $UF_6$ in product streams. Gravimetry may not be applicable for plutonium analysis because only $PuO_2$ is present in an acceptable for and it is hygroscopic. The amount and rate of water adsorption is dependent upon the ignition temperature [6].

## 3.2 Spectrophotometric Methods

Compounds or complexes in solution will absorb light of a specific wavelength in quantities proportional to the concentration of the measured species. Specificity is a function of the sharpness of the absorption bands, specificity of reagents, other elements or compounds present, and the quality of the monochromators. Specificity can be improved using preliminary separations, masking agents, and pH controls [6].

Spectrophotometric methods are of limited use for measuring uranium and plutonium in fuel-cycle materials due to the non-specificity of reagents for uranium in the presence of plutonium and because of the nuclear reaction products such as americium, neptunium, and the fission products. Separation of these radioisotopes requires more in-depth time consuming separations [6].

## 3.3 Electrometric Titration Methods

Oxidation-reduction reactions can be used to determine both uranium and plutonium products with high precision. There are three types of electrometric methods classified by how end-points are detected: amperometric, coulometric, and potentiometric [6].

Potentiometric titrations are based on measuring the change in potential of the system as a component is removed by oxidation or reduction. This technique is used to measure final products in the nuclear fuel cycle of $U_3O_8$, $PuO_2$, or $Pu(NO_3)_4$ [6].

Amperometric titrations measure the change in current between two electrodes maintained at a constant potential as titrant is added. The technique is limited by the accuracy of the inflection point measurement [6].

Coulometry can be used to determine uranium and plutonium in solution and is based on the principle that the weight of a substance oxidized or reduced at an electrode is proportional to the quantity of electrical charge passed through the electrode. Both uranium and plutonium are titrated in the same sample without separation by performing successive titrations at different potentials. The sample size of coulometric titrations is generally smaller than that needed for either potentiometric or amperometric titrations. The determination of plutonium requires many considerations and is generally not determined using this technique [6].

## 3.4 Fluorometry

Fluorometric determinations are applicable to low concentrations of uranium. It is not applicable to Pu. Fluorometry is based on the principle that uranium fluoresces when excited by ultraviolet light. Samples are generally evaporated and fused in a flux. Samples are generally fused in a carbonate flux or a NaF flux. Carbonate fluxes tends to provide better analytical precision although fluoride fluxes provide better uranium sensitivity. However fluoride fluxes are sensitive to flux temperature and cooling conditions. Most of the transition elements will interfere through quenching or enhancement [6].

Fluorometry evolved as the standard method for determining small amounts (1-100 ng) of uranium. High-throughput, off-line measurements of uranium in waste streams are made by processing samples in the analytical laboratory [6].

## 3.5 X-Ray Fluorescence

This technique is used primarily to measure solutions from the reprocessing of spent fuels but is applicable to actinide analysis at all stages of the fuel cycle. The techniques are sensitive, accurate, and capable of measuring microgram quantities of material to relative accuracies of about 1%. The typical analysis times are short ($\leq$ 0.5 h). The predominant source is the x-ray generator; however using radioisotopes is more common because the solid-state detector to measure the lower-intensity x-rays are readily available. Both uranium and plutonium in solution can be measured by wave-length and energy-dispersive detection systems. Wavelength dispersion has high resolution but low efficiency while energy dispersion is more efficient but has poorer resolution. Energy dispersion using Ge(Li) or intrinsic germanium detectors is required for measuring actinide K-series x-rays. To reduce matrix sensitivity, samples are often evaporated as thin film which reduces scattered background compared to the sample allowing for increased sensitivity and decreased counting times [6].

## 3.6 X-ray Absorption Edge Densitometry (K-edge)

Transmitted intensity through the sample is measured for two x-rays or gamma rays (selected above and below an absorption edge for the element being determined). This is an element specific method that can be used in time, at-line or off-line to measure uranium and plutonium in intermediate process and final product solutions [6].

K-edge densitometry has a limited dynamic range and cannot be used for a precise plutonium concentration in the presence of a large excess of uranium [6].

## 3.7 Alpha Spectrometric Methods

The measurement is based on the measurement of the alpha-radiation intensity of the sample. The alpha particles are ejected with discrete energies for uranium, neptunium, plutonium and americium isotopes. The energies are 4-5.5 MeV. This method is not quantitative unless prepared as a thin, dry film because absorption of water and self-absorption of the sample occurs. Detectors used for alpha spectrometry include standard radiation instruments such as proportional counters, scintillation detectors, and solid state devices. Special techniques were developed for the PUREX process streams where the detector is in direct contact with the alpha radiation sources [6].

## 3.8 Mass Spectrometric Methods

Mass spectrometry currently provides the most accurate isotopic analysis even in the presence of fission products. The isotope dilution technique provides an overall accuracy of 0.3-1% for the measurement of total uranium and plutonium in dissolver solutions [6].

Thermal-ionization mass spectrometry (TIMS) is used to determine the amount of each isotope of uranium and plutonium and is used to measure the total uranium and plutonium in accountability-tank samples. Isotope-dilution mass spectrometry is used for high-precision/high accuracy measurements of plutonium and uranium in tanks. Sample preparation involves: 1) dissolving and diluting with $HNO_3$, 2) for isotope-dilution mass spectrometry, spiking part of the diluted sample with accurately known amounts of U-233 and Pu-242 or Pu-244, 3) oxidizing Pu to hexavalent state, 4) sequentially separating fission products, plutonium and uranium by anion-exchange or solvent extraction, 5) transferring aliquots of the separated uranium and plutonium fractions to separate mass spectrometer filaments [6].

In TIMS, the light isotopes are evaporated and ionized preferentially, relative to the heavier isotopes of an element. The temperature-dependent effect is a function of the mass, sample size, and time. The abundances of major isotopes are determined with RDSs of 0.01 to 0.02%. High gamma-radiation levels limit the mass-spectrometric analysis of dissolver solutions to extremely small samples or to samples purified in shielded facilities [6].

# 4. TMI SAMPLE PREPARATION

TMI-2 samples were dissolved using a pyrosulfate fusion technique in a closed system. Iodine-129 tracer was added to the intact sample before dissolution, and Sr-90 was added after dissolution. This technique was used to allow measurement of the I-129 content of the sample.

Based on communications with D.W. Akers [5], corium samples that were larger in size were processed through several steps including: grinding to get samples 5-10 mg up to a gram maximum, a sequential dissolution beginning with nitric acid, then followed by hydrofluoric acid. Some samples were leached using a potassium permanganate solution and sometimes a sodium or ammonium (alkaline) permanganate solution was used. The main step in all the analytical processes was the pyrosulfate fusion**. Dr. Akers said that he would provide the exact steps on his return to work in late September 2013.**

Nitric acid was used to oxidize metals and alloys to soluble nitrates and the hydrofluoric acid was used to get rid of any silicates and dissolve the oxides of Nb, Ta, Ti and Zr. Standard pyrosulfate fusions were used for nuclear accountability is described below.

For pyrosulfate fusions to be successful, the sample must be oxidized to ensure that the sulfides, metals, and organics contain chemically bound oxygen or has been removed. Fusion samples only work if the sample has chemically bound oxygen such as oxides, carbonates, and silicates. A crucible (generally platinum, quartz, or porcelain for uranium and plutonium analysis) is filled half way with the sample mixed with a flux (potassium sulfate or sodium sulfate). The crucible is heated slowly and evenly to prevent ignition of the sample before the reaction with the molten salt will occur. The crucible and the ingredients inside are taken up to a fusion temperature of up to red heat. Once the salt is melted, the melt is swirled gently to monitor the reaction. The fusion continues until visible signs of the reaction are completed (e.g. formation of gases, foaming, fumes, etc). Usually a clear melt indicates the completeness of the sample decomposition. The melt is swirled during cooling to spread it over the inside of the crucible. Thin layers of salt on the sides of the crucible will crack and flake into small pieces during cooling making them easier to dissolve. Once the fusion has reached room temperature, it is dissolved with a dilute sulfuric or hydrochloric acid to avoid hydrolysis and precipitation of titanium and zirconium. Niobium and tantalum may precipitate but concentrated sulfuric acid, tartaric acid, ammonium oxalate, hydrogen peroxide or hydrofluoric acid can be added to prevent the precipitation. Mercury and the anions of volatile acids are generally volatilized during the fusion.

# 5. CONCLUSIONS

The destructive assay of samples obtained from the high temperature ceramic debris containing much of the destroyed and intact fuel rods and assemblies required innovative techniques. These samples were used to obtain quantifiable data that was used to describe the nuclear material accountancy of the destroyed TMI-2 nuclear reactor. The estimated temperatures at various regions of the core, in addition to recreations of the nuclear reactor accident allowed for characterization of many of the volatile, medium volatile and high volatile fission products. Sampling of the core itself and the debris that remained around the destroyed core provided an understanding of what happened during the accident. Unpublished work provided through communications with Dr. D.W. Akers, provided the destructive assay techniques used for material accountancy of the debris and core samples with the key component, being the pyrosulfate fusions that were performed after step by step

sizing and preconditioning techniques. These or similar techniques, can be utilized for nuclear material accountancy at the destroyed Fukushima Daiichi nuclear reactor in Japan.

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