Elemental and Radiological Characterization of Residue on the Surface of PRR-1 TRIGA Fuel Cluster Assembly

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Abstract

The Philippine Research Reactor-1 (PRR-1) of the Philippine Nuclear Research Institute (PNRI) has slightly irradiated Training Research Isotope General Atomics (TRIGA) nuclear fuel rods that have been stored in a wet storage tank for three decades. In support of the re-operation of PRR-1 as a subcritical assembly, which will reuse the TRIGA fuel rods, residues collected from the fuel cluster shrouds were characterized to ascertain the integrity of the fuel. The elemental composition of the residue samples was determined via wavelength dispersive X-ray fluorescence spectroscopy (WDXRF), while radiological characterization of potential alpha, beta, and gamma contamination was performed using a radiation counter. Gamma spectrometry was also carried out for water samples obtained from the fuel storage tank to determine if the water contains any radioactive materials that are beyond normal levels. Results indicated that residues collected on the fuel cluster shrouds were aluminum oxide while radiological contaminations were found to be below the values for surface and water contamination based on the Code of PNRI Regulations Part 3. These results demonstrated that although the fuel cluster shroud had some level of oxidation, there is no evidence that the integrity of the TRIGA fuel cladding has been compromised, thus confirming its suitability for repurposing.

Keywords*:* aluminum oxide, fuel storage tank, PRR-1, TRIGA fuel, water quality

1. Introduction

Claddings used in western designed research reactors use aluminum alloys such as aluminum 1100 or 6061 grades (International Atomic Energy Agency [IAEA], 2009). Aluminum has attractive properties such as good heat removal, reduced heat generation and low neutron absorption cross-section. It also has physical properties that are suitable for structural materials in nuclear reactors such as ductility, machinability, castability and weldability (Farrell, 2012). Aluminum has good resistance to aqueous solution due to the formation of self-restoring films of aluminum hydroxide and its near insolubility with water. However, aluminum has weak abrasion resistance and is prone to localized corrosion such as galvanic and pitting corrosion (IAEA, 2011).

In the Philippine setting, the Philippine Research Reactor-1 (PRR-1), which achieved its first criticality in 1963, is the first and only nuclear facility that was operated in the Philippines. The facility was originally built as a 1 MW material test reactor (MTR) type research reactor designed by General Electric Company. The original PRR-1 fuel had aluminum cladding and other reactor components were also made of aluminum. In 1984, the PRR-1 was converted and upgraded into a 3 MW TRIGA type reactor designed by General Atomics Inc. The converted PRR-1 TRIGA fuel use Incoloy 800 and Inconel 600 as cladding and fitting, respectively. To fit the rod-shaped TRIGA fuel in the original core box of PRR-1, fuel cluster shrouds were used to load the fuel in clusters of four (General Atomics Technologies Inc., 1987; IAEA, 2016).

The converted PRR-1 was operated at 3 MW for 5 h, which initially confirmed successful conversion. However, after the operation test, several technical issues were identified which led to the extended shutdown of the facility. The slightly irradiated PRR-1 TRIGA fuel rods, encased in cluster shrouds, were eventually transferred and stored in a wet storage tank in 1998. Since then, to maintain the integrity of the fuel rods until such time that its endpoint has been determined, the water in the storage tank has been maintained through a deionizer system. The deionizer system purifies the water in the fuel storage tank through filtration and removal of ions.

In 2014, it was decided to reuse the TRIGA fuel rods in a subcritical assembly to re-establish the capability of the Philippines in nuclear science and technology (Asuncion-Astronomo *et al*., 2019). To verify the suitability of the fuel rods for this purpose, a visual inspection of the rods was conducted in 2017. Inspection results reported that the fuel rods are still in good to excellent condition. However, it was also observed during the mentioned inspection that some fuel rods have residues on the cladding surface (Nuclear Reactor Operations Section [NROS], 2017). Further observations uncovered that white residues were also present in some parts of the fuel cluster shrouds, which warranted further investigation.

This paper presents the results of the work performed to characterize the residues obtained from the fuel cluster shroud. The characterization involved determining the chemical composition and measuring the level of radioactivity present in residue samples to exclude the possibility of fuel cladding corrosion and fission product leakage. The main motivation for this work was to confirm that the integrity of the TRIGA fuel cladding has been maintained after more than three decades in wet storage and to demonstrate its reliability for the PRR-1 Subcritical Assembly for Training Education and Research (SATER) facility that is currently under construction in the Philippine Nuclear Research Institute (PNRI), Quezon City, Philippines.

2. Methodology

Retrieval of fuel cluster shroud was done based on the methods reported in the IAEA fuel inspection report of PRR-1 TRIGA fuel (NROS, 2017). Residue samples were obtained by scraping onto the surface of the fuel cluster shroud using a spatula. To determine the elemental composition of the residue, samples were suspended in a mylar film and loaded to the X-ray fluorescence spectrometer (WDXRF) (Supermini 200 WDXRF, Rigaku Corporation, Tokyo, Japan) at 50 kV/200 W in EZ scan mode. Positive identification of elements from the sample was ensured based on the standards that were pre-loaded in the instrument's library.

Initial activity and dose rate of the fuel cluster shroud were measured using a surface contamination meter (CoMo 170, Strahlenschutz- Entwicklungs- und Ausrüstungsgesellschaft GmbH, Germany) and a survey meter (Thermo Scientific Radiameter FH 40 G-10, Thermo Electron GmbH, Germany), respectively. Figure 1 shows the general layout of the TRIGA fuel cluster assembly. Radiological characterization of the residue was carried out by preparing swipe samples using a 2.5-cm diameter circular filter paper. These filter papers were swiped entirely onto the surfaces of the handle (top), shroud (middle) and bottom-end fitting (bottom) parts (Figure 1) of the fuel cluster shroud. Swipe samples in quadruplicates were packed in individually-labeled resealable bags and were sent to the Radiation Protection Services Section (RPSS) of PNRI to detect possible alpha, beta and/or gamma contamination. Radiological analysis was performed using a scaler-ratemeter (Ludlum Model 2000, Ludlum Measurements Inc., United States) coupled with alpha counter and beta-gamma counter with details shown in Table 1.

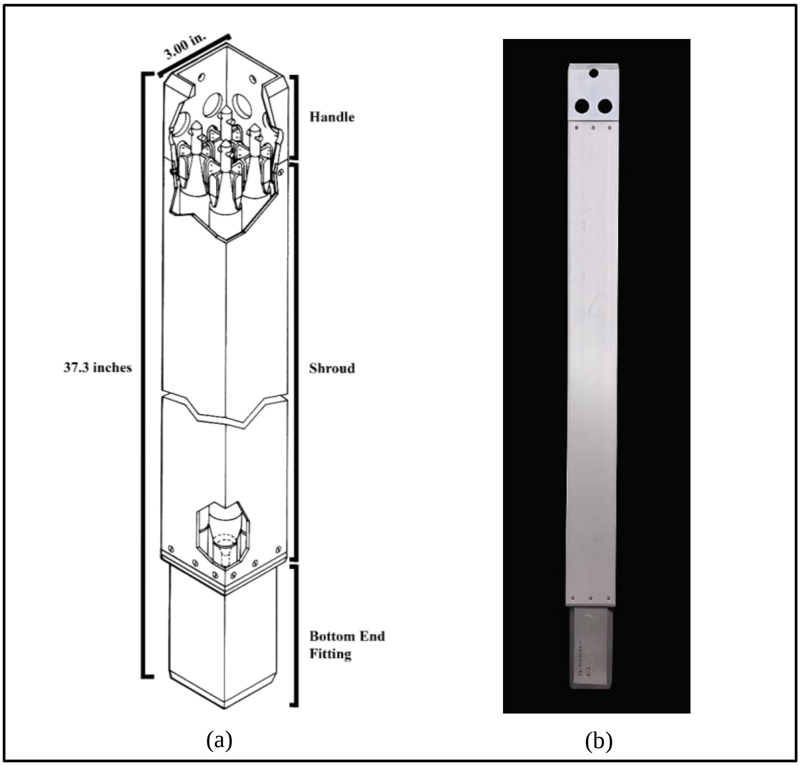

Figure 1. Diagram of fuel cluster shroud with TRIGA fuel inserted (a) and its actual photo (b)

Table 1. Technical specifications of Ludlum radiation counter

	Ludlum model 2000 alpha counter	Ludlum model 2000 beta-gamma counter
Efficiency	80.59% (against Am-241)	66.97% (against Cs-137)
Scaler model	Ludlum model 43-10	Ludlum model 43-10-4

Water samples from the fuel storage tank were also collected and placed in 1-L polyethylene terephthalate (PET) bottles. Samples were brought to the Nuclear Analytical Techniques and Applications Section (NATAS) of PNRI for gammametric analysis using a gamma counting system with high purity germanium (HPGe) detector (CPVDS30-15180, Tennelec, United States) linked to a detector interface module positive Ge (AMETEK ORTEC, United States) and digital signal processor (DSPEC jr 2.0, AMETEK ORTEC, United States) to detect the presence of long-lived radionuclides.

3. Results and Discussion

3.1 Elemental Characterization of White Residues

Figure 2 shows the residues collected from selected fuel cluster shrouds. The residue with a whitish appearance was analyzed to confirm its elemental composition, which is summarized in Table 2.

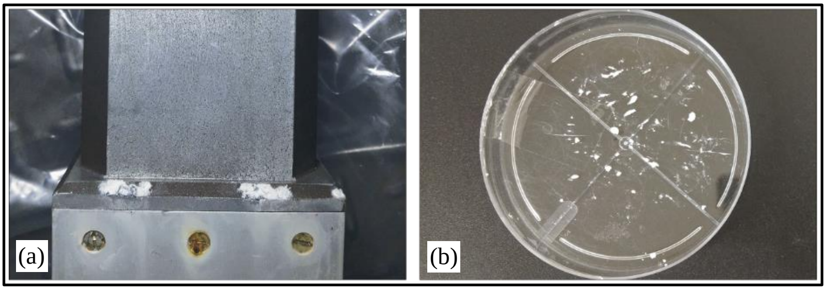

Figure 2. White residues found in (a) and collected from (b) the fuel cluster shroud

Table 2. WDXRF result of white residue sample

Component	Mass (%)
MgO	3.2469
Al_2O_3	52.6062
SiO_2	5.6015
P_2O_5	9.1762
SO_3	14.3025
Cl	0.9456
K_2O	1.3140
CaO	5.4365
Cr_2O_3	1.1256
Fe_2O_3	5.5994
NiO	0.5856

Primary element oxides found in the sample include Al_2O_3 (52.61%), MgO (3.25%) and SiO_2 (5.60%). The full WDXRF results (Table 2) also suggested the presence of other elements in the analyzed sample. The WDXRF spectrum for aluminum is shown in Figure 3. Based on these results, aluminum oxide had the highest concentration among other elemental components measured. It can be deduced that the white residues were mostly from aluminum oxide contribution. This can be attributed to the chemical reaction of aluminum with water to form aluminum oxides.

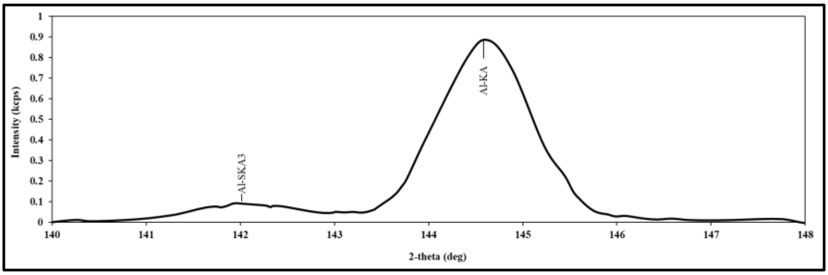

Figure 3. WDXRF spectra of the white residue sample

In an aqueous solution, the resistance of aluminum is manifested by its ability to form near insoluble self-restoring films of aluminum hydroxide (Farrell, 2012). Based on the safety analysis report and other PRR-1 technical documents, the fuel cluster shroud is composed of aluminum parts with stainless steel inserts (General Atomics Technologies Inc., 1987). This indicated that the residue cannot have originated from the fuel cladding because of the high corrosion and oxidation resistance of Incoloy 800 and Inconel 600 (Fulger *et al.*, 2009; Rao *et al.*, 2020; Li *et al.*, 2021). The formation of the white residue in the TRIGA fuel rod surface can be attributed to the disturbance of water and some loose residues, which adhere to its surface over time. Moreover, the aluminum contents of Incoloy 800 and Inconel 600 were less than 1% (Special Metals Corporation, 2004, 2008) compared with aluminum 6061 which had almost 100% (Table 3).

Table 3. Chemical composition of aluminum 6061
(The Aluminum Association, 2015)

Elements	Mass (%)
Al	99.99
Si	0.40-0.80
Fe	0.7
Cu	0.15-0.40
Mn	0.15
Mg	0.80-1.2
Cr	0.04-0.35
Zn	0.25
Ti	0.15
Others	0.15

Other components found on the residue can be linked to the presence of other inorganic elements from sources such as airborne material and leachates from other materials in the tank, which is similar to what was observed in a previous study (Aghoyeh and Khalafi, 2011). This can be corroborated by the conductivity data obtained from the internal water quality monitoring record of the PRR-1 facility (Figure 4).

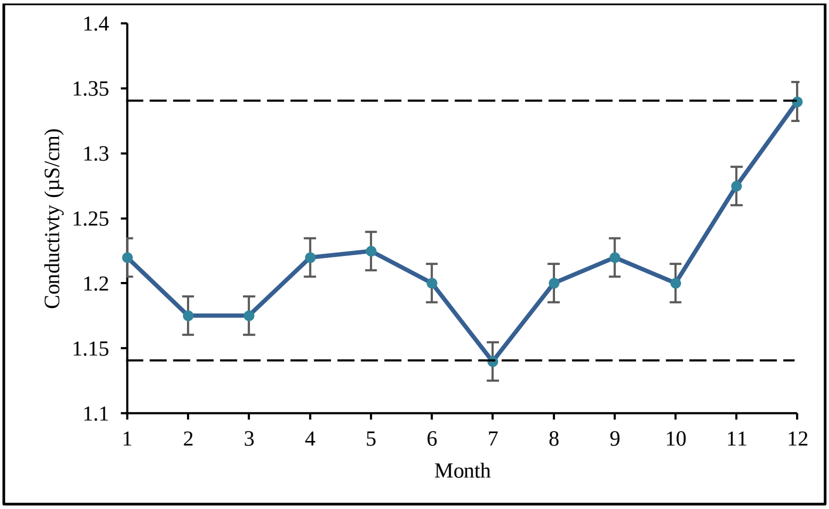

Figure 4. 12-month period conductivity values measured in 2020 for the water in the PRR-1 fuel storage tank

The values obtained for the conductivity in 2020 ranged from 1.14 to 1.34 μS/cm indicating the presence of trace amounts of foreign materials in the water of the fuel storage tank, which may explain the presence of other compounds listed in Table 2. A related study reported that corrosion is influenced by the condition of water in the pool such as high water conductivity, high concentration of aggressive chloride ions, presence of two or more different metal claddings (galvanic coupling) and presence of iron particles and other cathodic particles with reference to aluminum (IAEA, 2009; Aghoyeh and Khalafi, 2010). Further work must be done to confirm these initial findings.

3.2 Radiological Measurements for Fuel Cluster Shroud

The initial measurement of radiation from the fuel shroud was performed (Figure 5) and the measured values are shown in Table 4. The dose rate registered a reading of 1.54 μSv/h, which can be ascribed to the activation of the cluster shroud; the annual background reading in the fuel storage tank is approximately 0.223 μSv/h.

Table 4. Initial radiological measurements of the fuel cluster shroud

Fuel cluster shroud surface	Net counts (cps)	Activity (Bq/cm^2)
Handle (top)	~85.0	1.87
Shroud (middle)	~111.8	2.46
Bottom end fitting (bottom)	~115.4	2.54

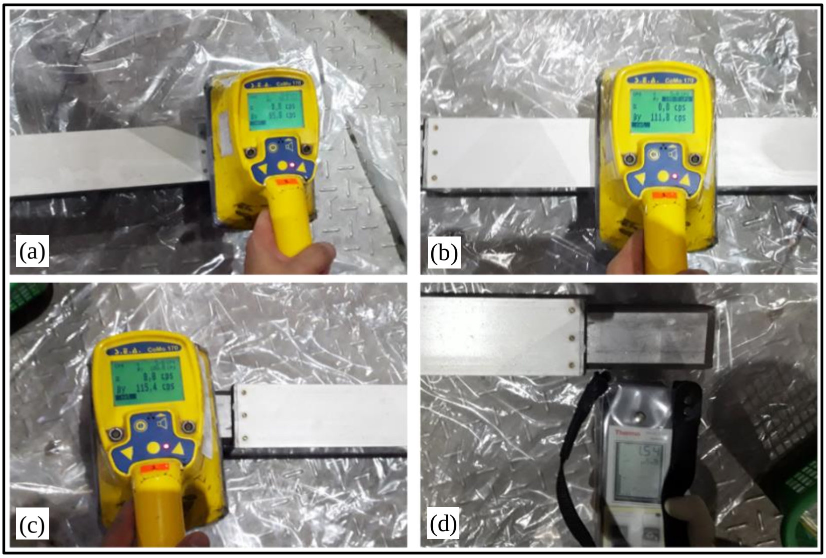

Figure 5. Contamination meter reading of the handle (a), shroud (b) and bottom-end fitting (c); dose rate at the bottom-end fitting (d)

The activity measured from the swipe samples was found to be significantly lower than the exempted value (Tables 5 and 6).

Table 5. Measured activities of swipe samples using an alpha counter

Sample ID	Activity (Bq/cm^2)	% difference from exempted value*
1.1	0.02	-175%
2.1	0.01	-187%
3.1	0.03	-164%
4.1	LBR	n/a
5.1	LBR	n/a

LBR – less than background, readings were subtracted with the background reading; *exempted value is 0.3 Bq/cm^2 based on Code of PNRI Regulations Part 3 (PNRI, 2004).

This asserted that there has been no removable contamination in the fuel shroud and that the reading from the contamination meter was most likely due to neutron activation of the components. This was highly plausible considering that the shrouds were also neutron-irradiated for 5 h at 3 MW power during the PRR-1's operation test after conversion.

Table 6. Measured activities of swipe samples using a beta-gamma counter

Sample ID	Activity (Bq/cm^2)	% difference from exempted value*
1.2	0.65	-129%
2.2	0.76	-119%
3.2	0.95	-104%
4.2	0.61	-132%
5.2	0.59	-134%

*Exempted value is 3 Bq/cm^2 based on Code of PNRI Regulations Part 3 (PNRI, 2004).

3.3 Radiological Analysis for Water Sample

The result of the gammametric analysis for potential fission products or long-lived radionuclides is presented in Table 7. The data indicated that there was no detectable activity of fission products and other long-lived radionuclides except for K-40, which is naturally occurring. This demonstrated that the PRR-1 TRIGA fuel cladding has remained intact; its integrity has been maintained throughout its storage time.

Table 7. Result of gammametric analysis of water sample taken in the fuel storage tank

Radionuclides	Result	Exempted value* (Bq/kg)
Cs-137	Less than LLD	10,000
Cs-134	Less than LLD	10,000
I-131	Less than LLD	100,000
Co-60	Less than LLD	10,000
K-40	10±1 Bq/kg	100,000
Tl-208 (Th-progeny)	Less than LLD	1,000
Ac-228 (Th-Progeny)	Less than LLD	1,000
Bi-214 (U-Progeny)	Less than LLD	1,000
Pb-214 (U-Progeny)	Less than LLD	1,000

LLD – lower limit of detection; *exempted values are based on Code of PNRI Regulations Part 3 (PNRI, 2004).

Compared with the values set by the Code of PNRI Regulations Part 3 (PNRI, 2004), the values reported in Tables 5 and 6 confirmed that the surface of the fuel cluster shroud has no removable surface contamination. For the water sample, the data presented in Table 7 showed that any radioactivity in the water is lower than detection limits. These results support the conclusion from the visual inspection of the TRIGA fuel that the fuel rods are either in good or excellent condition.

4. Conclusion

The white residues found in the TRIGA fuel rods were shown to be from accumulated oxides, which were predominantly aluminum oxides at 52.6% composition. Other elements found in the residue were attributed to trace amounts of ions in the water and the presence of other metal alloys in the fuel storage tank components. Radiological swipe tests confirmed that there was no removable contamination from the fuel shroud with measured surface contamination values that were significantly lower by 164 to 187% for alpha and 104 to 134% for beta-gamma in comparison with the exempted values based on Code of PNRI Regulations Part 3. Moreover, no detectable radiation was found from the radiological analysis performed on water samples from the storage tank. These indicated that the PRR-1 fuel cladding has been uncompromised and found suitable for reuse into a subcritical assembly.

5. Acknowledgement

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6. References

Aghoyeh, R.G., & Khalafi, H. (2010). Corrosion monitoring and determination of aluminium fuel clad of Tehran Research Reactor (TRR). Progress in Nuclear Energy, 52(2), 225-28. https://doi.org/10.1016/j.pnucene.2009.06.011

Aghoyeh, R.G., & Khalafi, H. (2011). Design of water purification system for Tehran Research Reactor spent nuclear fuels storage pool (wet storage). Progress in Nuclear Energy, 53(1), 119-124. https://doi.org/10.1016/j.pnucene.2010.07.011

Asuncion-Astronomo, A., Štancar, Ž., Goričanec T., & Snoj, L. (2019). Computational design and characterization of a subcritical reactor assembly with TRIGA fuel. Nuclear Engineering and Technology, 51(2), 337-44. https://doi.org/10.1016/j.net.2 018.09.0 25

Farrell, K. (2012). Performance of aluminum in research reactors. Comprehensive Nuclear Materials, 5, 143-75. https://doi.org/10.1016/B978-0-08-056033-5.00113-0

Fulger, M., Ohai, D., Mihalache, M., Pantiru, M., & Malinovschi, V. (2009). Oxidation behavior of Incoloy 800 under simulated supercritical water conditions. Journal of Nuclear Materials, 385 (2), 288-293. https://doi.org/10.1016/j.jnucmat.2008.12.004

General Atomics Technologies Inc. (1987). Safety analysis report for the 3-MW forced flow operation TRIGA conversion Philippine Research Reactor.

International Atomic Energy Agency (IAEA). (2009). Corrosion of research reactor aluminium clad spent fuel in water. Vienna, Austria: IAEA.

International Atomic Energy Agency (IAEA). (2011). Good practices for water quality management in research reactors and spent fuel storage facilities. Vienna, Austria: IAEA.

International Atomic Energy Agency (IAEA). (2016). History, development, and future of TRIGA research reactors. Vienna, Austria: IAEA.

Li, D.S., Cheng, G., Li, D., Zheng, Q., Gao, P., & Zhang, L. (2021). Oxidation resistance of nickel-based superalloy Inconel 600 in air at different temperatures. Rare Materials, 40, 3235-3240. https://doi.org/10.1007/s12598-018-1148-1

Nuclear Reactor Operations Section. (2017). PRR1-CD-17: Report on inspection of PRR-1 TRIGA fuel elements. Quezon City, Philippines: Philippine Nuclear Research Institute – Department of Science and Technology.

Philippine Nuclear Research Institute (PNRI). (2004). Standards for protection against radiation (Code of PNRI Regulations Part 3). Quezon City, Philippines: Philippine Nuclear Research Institute – Department of Science and Technology.

Rao, M.J., Shaik, R.U., & Buschaiah, K. (2020). Electrical discharge machining: A comparative surface integrity study for incoloy-800. Materials Today: Proceeding, 22 (4), 3286-3296. https://doi.org/10.1016/j.matpr.2020.03.290

Special Metals Corporation. (2004). Incoloy® alloy 800Ht. Retrieved from https://www.specialmetals.com/documents/technical-bulletins/incoloy/incoloy-alloy-800h-800ht.pdf

Special Metals Corporation. (2008). Inconel® alloy 600. Retrieved from https://www.specialmetals.com/documents/technical-bulletins/inconel/inconel-alloy-600.pdf

The Aluminum Association. (2015). International alloy designations and chemical composition limits for wrought aluminum and wrought aluminum alloys. Retrieved from https://www.aluminum.org/sites/default/files/Teal Sheets.pdf