INL/RPT-23-74755-Revision-0

Completion and Testing of a New High-Temperature Cell Holder to Support High Dose Rate Electron Beam Irradiations of Select Sulfur Chlorides (S_2Cl_2 and $SOCl_2$) for Advanced Low Temperature Chlorination of Zirconium-based Used Nuclear Fuel Cladding

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Idaho National Laboratory

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The Idaho National Laboratory (INL) Center for Radiation Chemistry Research (CR2) commissioned a high-temperature (≤ 700 °C) cell holder to support the advancement of a new sulfur chloride based technology for the chlorination and recovery of zirconium from used nuclear fuel cladding [1–3]. The current proposed process employs sulfur monochloride (S_2Cl_2) for the dissolution of zirconium alloy fuel cladding, and then thionyl chloride ($SOCl_2$) for the separation and purification of the resulting zirconium tetrachloride [3]. These chemicals are expected to receive significant radiation doses, and as such, a new high dose rate irradiation capability needed to be established to facilitate timely irradiations under more representative process conditions.

The bespoke high dose rate and temperature irradiation cell—designed and fabricated by Brookhaven National Laboratory (BNL)—was installed at the Idaho State University Accelerator Center (IAC) and tested under ambient and 400 °C temperature conditions with varying electron beam dose rates (15, 30, and 60 Hz 8 MeV pulses), as delivered by a 25 MeV S-band Varian (Palo Alto, CA, USA) 2500 linear accelerator (LINAC). The installed setup is shown in **Figure 1**.

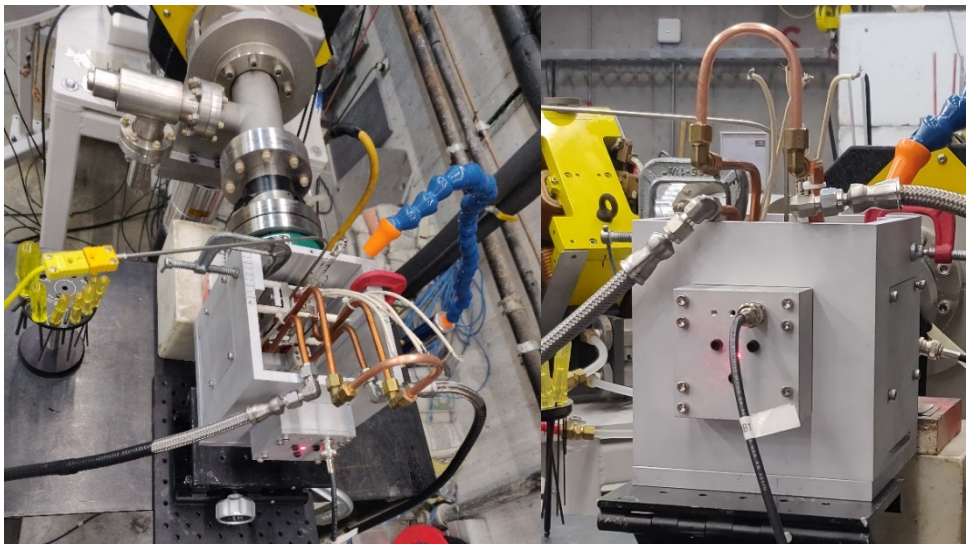

Figure 1. Images of the high-temperature sulfur chloride irradiation sample holder installed at the IAC electron beam line.

Ambient temperature experiments were performed using flame sealed vials of $SOCl_2$, with the intention of establishing the new setups alignment, electron beam profile, and dose rate (Gray per electron pulse), as determined by both physical (HD-V2 radiochromic film) and

chemical (Fricke solutions [4]) dosimeters. Alignment of the new sample holder was optimized with a laser (the red dot shown in **Figure 2**) calibrated to the accelerator's electron beam path. Confirmation of alignment and determination of the LINAC's beam profile and unattenuated dose rate (~300 Gy per pulse) was achieved using the HD-V2 radiochromic film (shown in **Figure 2**), which was taped to an aluminum plate and positioned in front of our sample window.

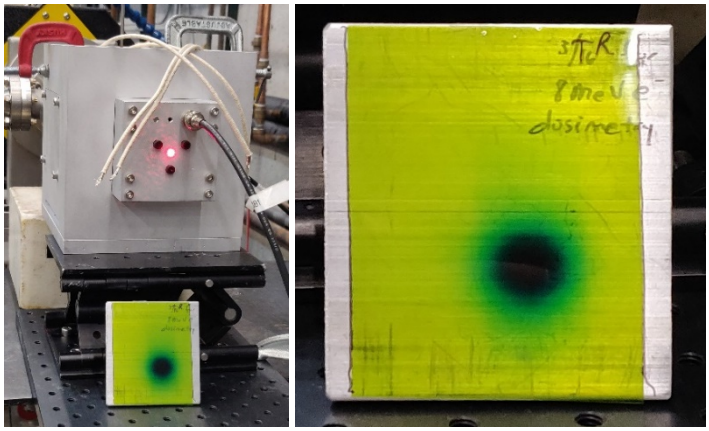

Figure 2. Typical images of the irradiated HD-V2 radiochromic film. The darkened spot highlights the beam's profile incident upon the new sample holder's window.

Once aligned, chemical dosimetry, using Fricke solution, was then performed to determine the actual dose rate to be experienced by our $SOCl_2$ samples, as a function of volume. A Starna Scientific Ltd. (Ilford, United Kingdom) 1.0 cm optical pathlength, quartz cuvette was filled with 3.8 mL Fricke solution (1 mM $FeSO_4.7H_2O$ and 1 mM NaCl in 0.4 M H_2SO_4). This volume corresponded to the total volume of the cuvette used and the approximate volume of $SOCl_2$ in the flame sealed vials.

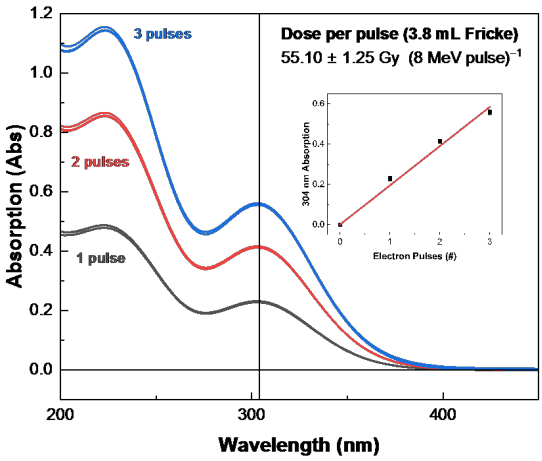

Figure 3. Absorption spectra from the electron beam irradiation of Fricke solution loaded in quartz cuvettes similar to those used for the irradiation of flame sealed $SOCl_2$ samples. *Inset:* Dose rate determination using the 304 nm peak absorption as a function of the number of electron pulses. Solid line is a weighted linear fit to transformed data, affording a dose rate of 55.10 ± 1.25 Gy per pulse of 8 MeV electron to 3.8 mL of Fricke solution, $R^2 = 0.9949$.

The cuvette was rinsed and refilled with fresh Fricke solution following each irradiation experiment, which comprised of one, two, and three electron pulses in triplicate. Irradiated Fricke solution samples were then analyzed using a Cary 6000i UV-vis-nIR spectrophotometer (Agilent, Santa Clara, CA, USA) back at INL, affording the spectra shown in **Figure 3**. The

absorbance maximum of iron(III) at 304 nm was plotted as a function of the number of electron pulses to give an average dose rate of 55.10 ± 1.25 Gy per pulse of 8 MeV electron (**Figure 3** *Inset*).

Under these electron beam conditions and at ambient temperature, six flame-sealed $SOCl_2$ samples were successfully irradiated, covering a dose range of 1.2–8.8 MGy. During these irradiations, sample cells were maintained at less than 50 °C, with and without water cooling, thereby covering the range of ideal process operating temperatures [3]. Water cooling allowed for more electron pulses per unit time prior to reaching our self-imposed 45 °C threshold, above which the risk of cell rupture due to sample volatilization significantly increased.

A series of high temperature (400 °C) irradiations were also successfully performed to evaluate the new sample holders heating capabilities. These experiments were not performed with sulfur chloride samples to avoid cell rupture risks. High temperature irradiations demonstrated that the cell holder can reach and maintain elevated temperatures and that high dose rate electron beam irradiation did not lead to radiation-induced cell rupture under these conditions.

Overall, a new high dose rate and temperature cell holder has been designed, built, and successfully tested in support of advanced low temperature chlorination technologies for used nuclear fuel reprocessing. This capability is now available to the Material Recovery and Waste Form Development (MRWFD) campaign for future irradiation studies.

ACKNOWLEDGEMENTS

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