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ANL-25/42

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Chemical and Fuel Cycle Technologies Division

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Van de Graaff Irradiation Studies of Oxygen Sensor and Hydrated Zirconia Sorbent

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ABBREVIATIONS

HZO	Hydrated zirconia
RGA	Residual gas analyzer
ZrO_2	Zirconium dioxide

1 INTRODUCTION

Commercial-scale production of Mo-99 demands a facility-wide assessment of radiation-induced degradation across process equipment, instrumentation, and purification media. Key factors—total ionizing dose, dose rate, radiolysis-driven chemistry, thermal loads, activation, and any neutron-related effects—should inform material selection, shielding, and component layout. Purification materials (sorbents, resins, filters, seals, housing) require particular attention to ensure that irradiation does not alter selectivity or capacity, generate fines, or introduce leachables that could compromise Mo-99 purity or downstream Tc-99m generator performance. Dose mapping, accelerated irradiation testing, and studies of extractables/leachables together provide the basis for setting maintenance, calibration, and replacement intervals and for qualifying materials that retain mechanical integrity, chemical compatibility, and radiopurity over their service life.

During irradiation, water radiolysis produces hydrogen and oxygen in the process headspace. Continuous monitoring of both gases is necessary to operate the catalytic H_2/O_2 recombiner, which converts them back to water, stabilizes solution chemistry, limits pH drift, helps maintain uranium concentration by offsetting water losses, and preserves redox conditions that support consistent Mo-99 purification. Because this control strategy relies on accurate oxygen measurements, it is essential to establish calibration intervals, inspection routines, and end-of-life criteria for headspace oxygen analyzers. To quantify radiation-induced drift, response degradation, and failure modes—and to establish appropriate maintenance cycles—oxygen sensors were irradiated under conditions representative of scaled Mo-99 production.

Hydrated zirconia (HZO) serves as a final polishing sorbent in the LEU Modified Cintichem process to remove residual impurities and meet stringent Mo-99 specifications. Given its position near the end of the purification train, the radiation stability of HZO—and any irradiation-induced effects on molybdenum chemistry—is critical to sustaining high recovery yields and product purity.

This report presents results from radiation-stability tests of oxygen sensors and HZO using a 3 MeV electron Van de Graaff accelerator under process-relevant conditions.

2 EXPERIMENTAL

2.1 IRRADIATION OF OXYGEN SENSORS WITH X-RAY CONVERTER

Radiation testing of the oxygen sensor was performed using bremsstrahlung photons generated by a platinum/gold (Pt/Au) X-ray converter mounted at the beam exit, as shown in Figure 1. Irradiation was conducted at a standoff distance of 1 in. from the converter's surface; the converter's total material thickness was 1 mm. To characterize the photon field and establish operating setpoints, the relationship between the dose rate at a 1-in. distance and accelerator beam current with the converter installed was measured and is presented in Figure 2. Dose measurements were obtained with a Radcal Corporation Model 9010 radiation monitor controller coupled to a Radcal Model 9060A ionization chamber, and the resulting dose–current calibration was used to verify beam conditions and guide the selection of irradiation parameters for the sensor tests.

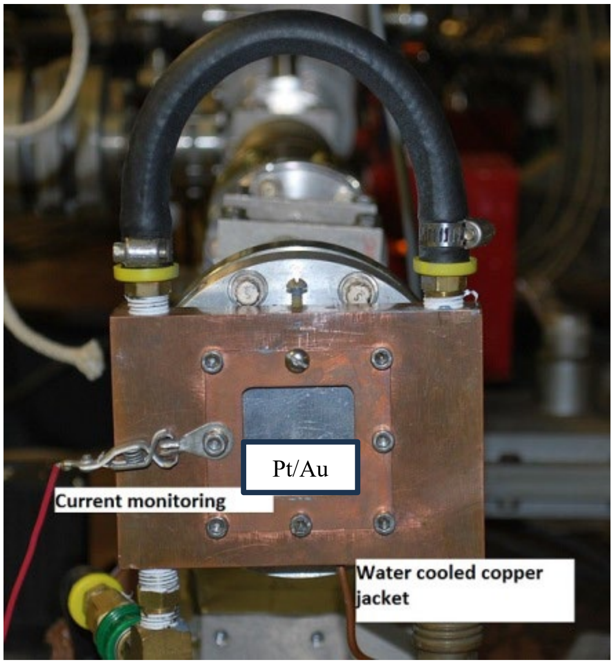

Figure 1. Platinum/gold water-cooled x-ray converter installed at the end of the beamline.

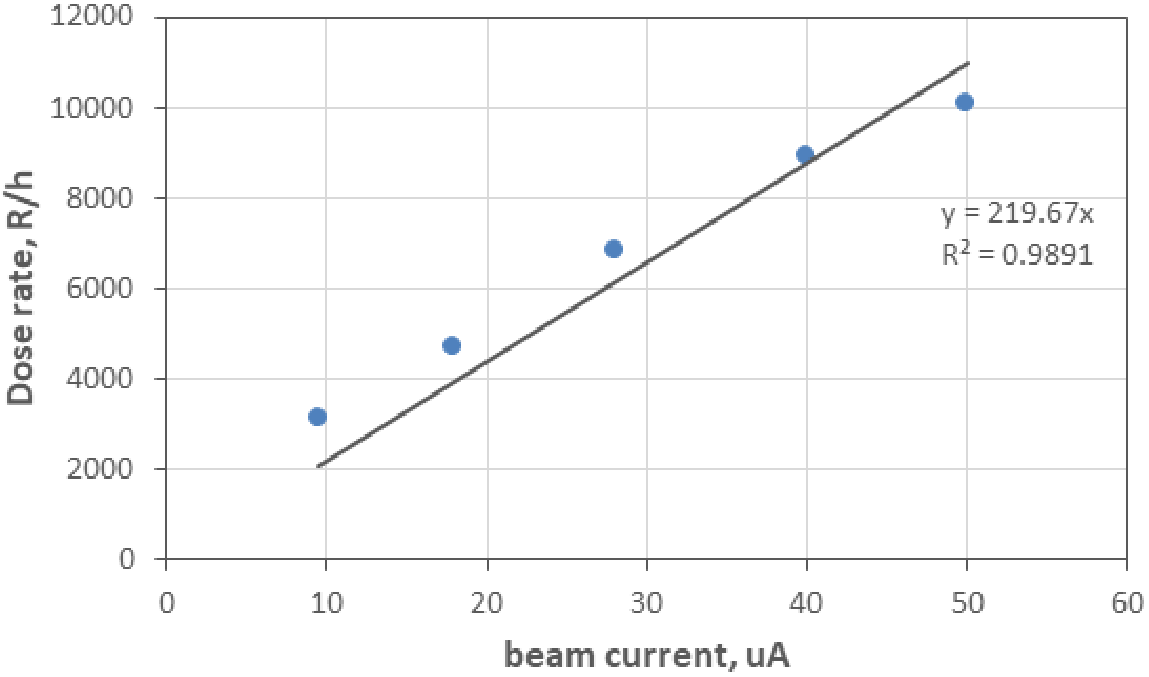

Figure 2. Platinum/gold x-ray converter calibration data. Linear relationship between the current and dose was determined from X-ray irradiations using a Radcal Dosimeter.

Irradiations were performed using a 40-uA beam current on the converter, resulting in a 9000 R/h dose rate at the oxygen sensor location.

Oxygen sensor description and testing setup

The oxygen sensor (SST OXY-LC-V25-455) was interfaced with a signal-conditioning board (PN OXY-LC-V25-455). The sensor employs a zirconium dioxide (ZrO_2) solid electrolyte with porous platinum electrodes to provide 0.1–0.9 volts. A signal-conditioning board converts this voltage into a linear 0–10 V DC output proportional to oxygen concentration over the 0.1–25% O_2 range [1]. At elevated operating temperatures, ZrO_2 conducts O^{2-} ions; under a constant DC drive across the porous Pt electrodes, oxygen ions are transported through the electrolyte and oxygen is liberated at the anode in proportion to the transported charge, while a Nernst potential also develops when different oxygen partial pressures exist across the electrodes. In practice, the board maintains the sensor at its operating temperature, controls the electrochemical pumping, and linearizes the response to yield the specified 0–10 V output. The manufacturer recommends a 200-hour initial warm-up for the best stability, and only a single-point calibration in air is required to set the span.

For irradiation, the sensor was mounted in a stainless-steel flow chamber with dedicated inlet and outlet (Figure 3). A certified standard mixture containing 9.96% O_2, 88.07% N_2, and 1.966% Ar was delivered at 50 mL/min during each exposure using an Omega FMA5506A-ST mass flow controller; the flow was verified with a Brooks 4800 flowmeter, and system pressure was monitored with an Omega Engineering pressure transducer. The chamber and sensor were positioned 1 in. from the gamma/X-ray converter at the end of the Van de Graaff beamline (Figure 4). Sensor output voltage was logged continuously during irradiation and compared against a calibrated Pfeiffer OmniStar QMG 220 quadrupole mass spectrometer (gas analyzer) sampling the exhaust stream to verify gas composition. Because the calibration pressure differed from the test pressure, a pressure-compensation factor was applied to the sensor output, $f = P_{cal}/P_{test}$, consistent with the sensor's proportional dependence on oxygen partial pressure.

Figure 3. Oxygen sensor and housing.

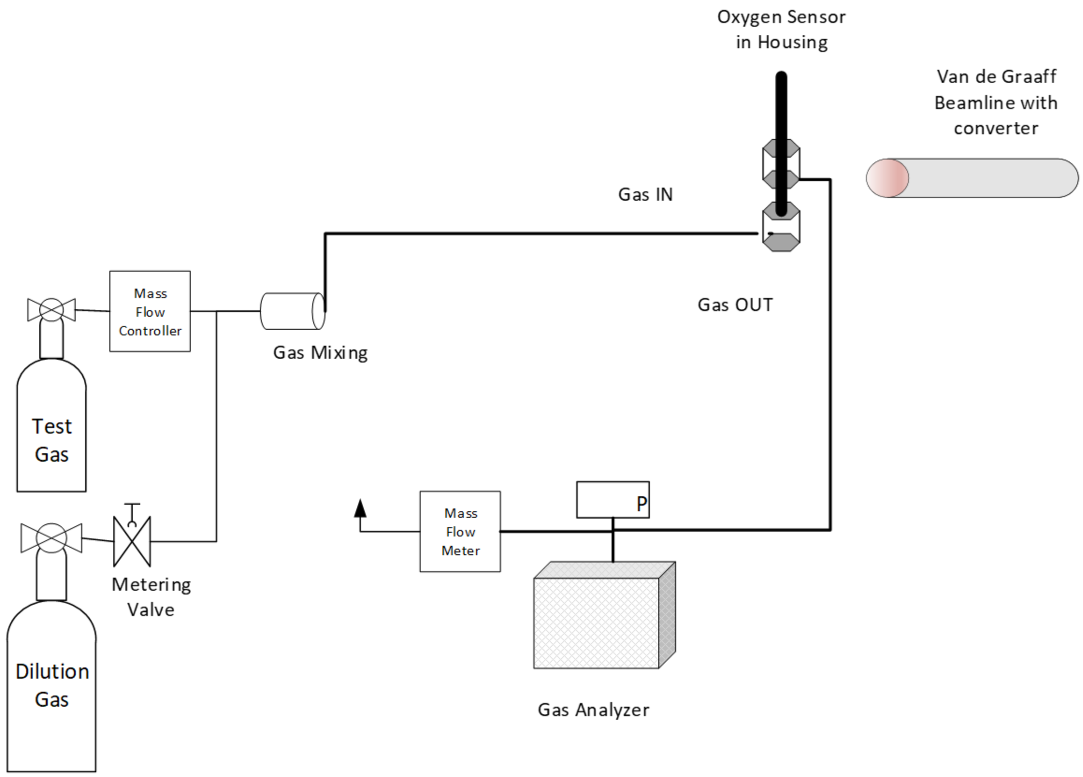

Figure 4. Diagram of irradiation experiments.

2.2 ELECTRON BEAM IRRADIATIONS OF ZRO SAMPLES

All electron irradiations were carried out with the 3-MeV Van de Graaff beam at a fixed geometry, with the irradiation point 15 in. from the accelerator exit window. Absorbed dose was quantified using oxalic acid dosimetry [2] (Figure 5) following the procedure in [3]: for each run, 1 mL of 0.6 M oxalic acid was irradiated and then titrated with 0.1 N NaOH using phenolphthalein to determine the residual acid, from which the delivered dose was calculated on the basis of radiolytic decomposition.

Ten irradiations were performed over a range of beam currents, with the Van de Graaff current measured at the collimator in front of the samples and logged throughout each exposure; average currents spanned 4.96–11.4 µA, and irradiation times were 15–40 min, depending on the target dose.

The resulting calibration (dose versus the product of beam current and irradiation time) was linear within the tested range, enabling prediction of total dose for arbitrary combinations of current and time; the slope of this relationship yielded a dose rate of 0.256 Mrad/(µA·min). Thermal stability was maintained by directing air across both sides of the test tube to prevent overheating at the stated standoff distance. Beam profile measurements confirmed good field uniformity at the sample location, and the corresponding dose variation within 1 in. of the beam center was measured to be less than 10% (Figure 6).

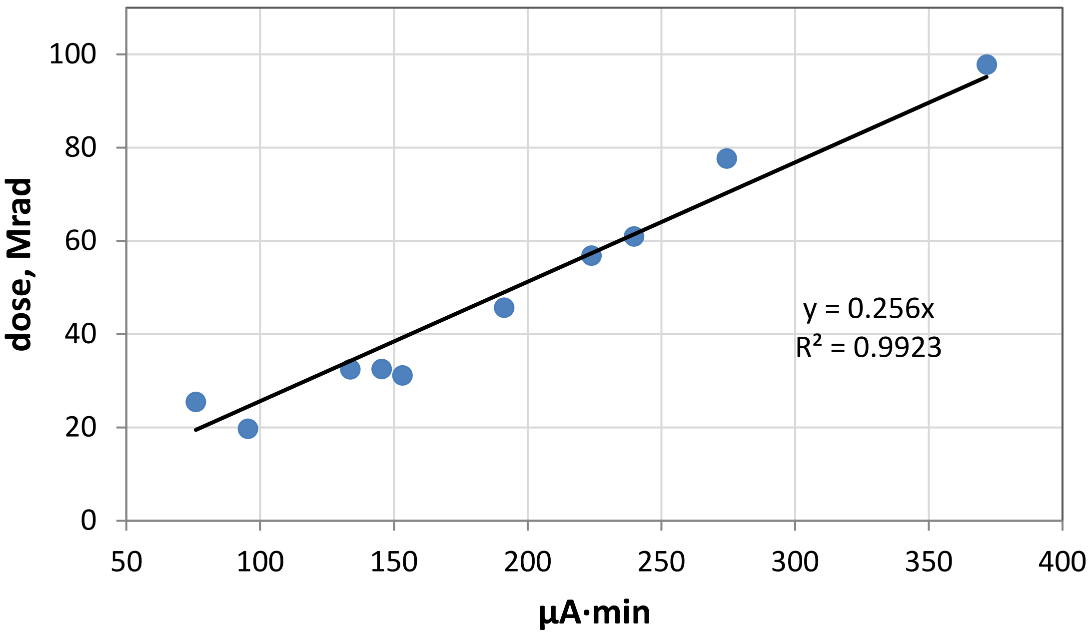

Figure 5. Oxalic dosimetry data.

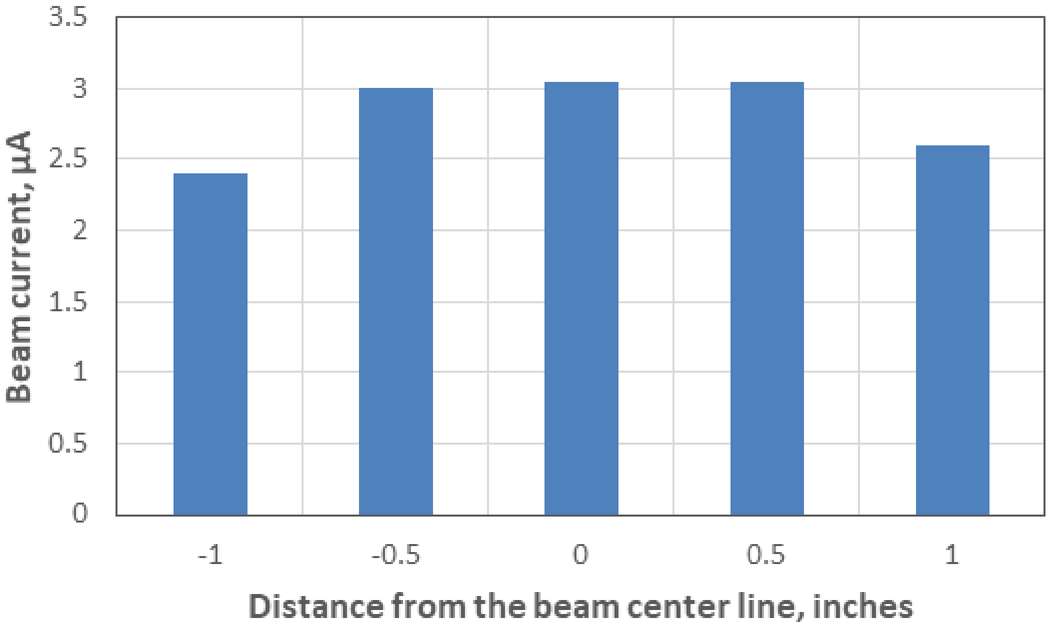

Figure 6. Electron beam profile at 15 in. from the window.

The sample was mounted in an aluminum holder on a vertically adjustable stage to center it in the electron beam and was air-cooled using compressed air directed across the sample. The holder was positioned 15 in. from the beamline exit window; photographs of the setup are shown in Figure 7. A water-cooled copper collimator upstream of the sample defined the field, limited beam spread, and ensured reproducible irradiation conditions, while a thick copper block downstream served as a beam stop to absorb the transmitted beam and reduce scatter. The thermal checks across beam currents showed that, at 10 µA, the sample temperature stabilized at 24°C under the implemented cooling. Alignment was verified with a laser level to place the sample precisely on the beam axis and to confirm that the collimator aperture did not clip the beam, ensuring uniform exposure of the entire sample surface.

For these irradiations, the Van de Graaff accelerator operated at 3 MeV, delivering approximately 10 µA at the shutter and 6.4 µA at the collimator; at a 15-in. standoff, the beam exhibited a uniform profile across the collimator aperture. Samples contained in open-top quartz vials were irradiated to total doses of 60, 120, and 240 Mrad.

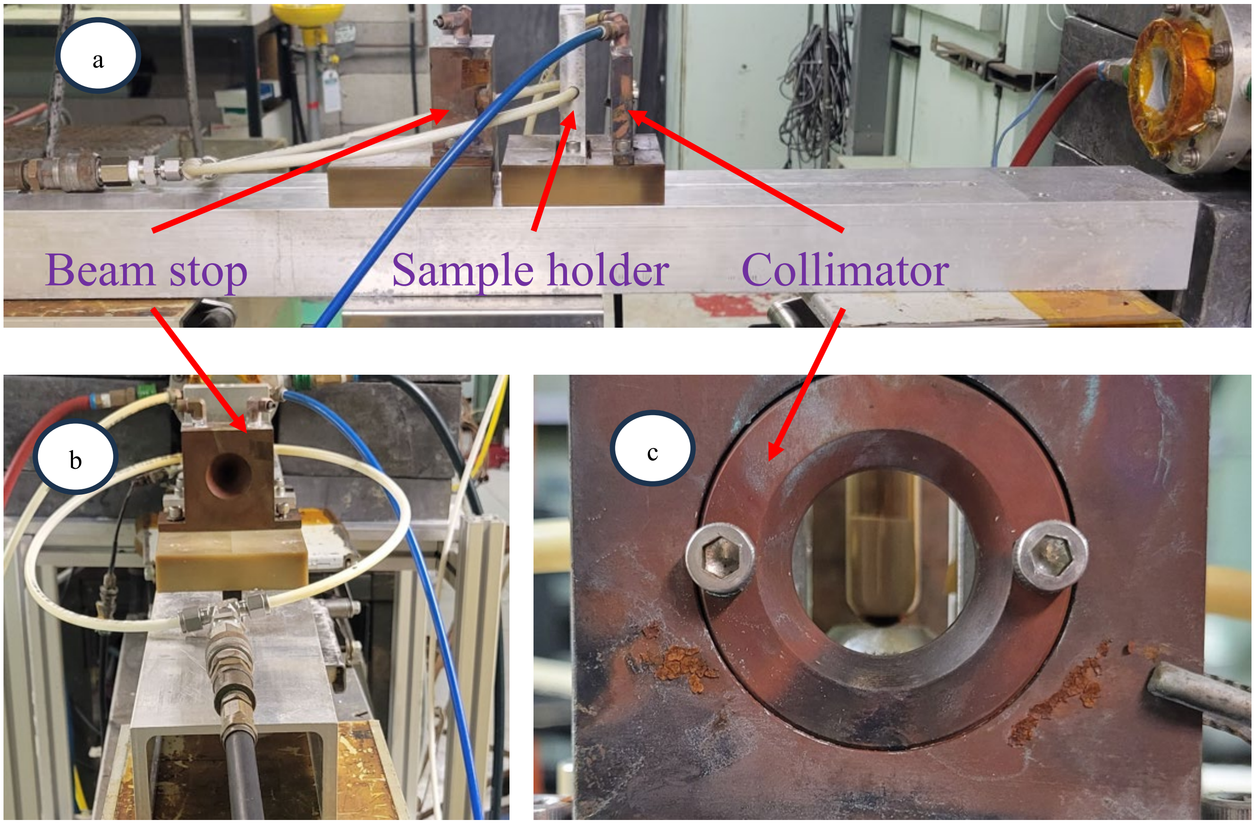

Figure 7. Irradiation setup used for irradiation of liquid samples: (a) side view, (b) back view, (c) front view.

3 RESULTS AND DISCUSSION

3.1 OXYGEN SENSOR TESTING

Across five irradiations at an accelerator current of approximately 40 µA, delivering a cumulative 14.2 Mrad, the zirconia oxygen sensor remained functional and provided repeatable results, exhibiting a consistent but positive bias with percent recoveries of 104–113% relative to the test standard, while an independent Pfeiffer gas analyzer confirmed the delivered compositions at 98–100% recovery. Prior to irradiation, calibration in air at 23°C (assumed 20.7% O_2) produced an output of 8.28 V, establishing a span of 0.40 V per % O_2; a pressure-compensated check yielded 102% recovery (gas analyzer: 99%), providing a sound baseline. During and after the first irradiation, indicated recoveries increased modestly to 104% and 108%, and subsequent irradiations were similar (111–112%); this behavior is consistent with a small positive offset and slight drift expected during the manufacturer-recommended ~200-h warm-up. Recalibration before the fifth irradiation brought the readings closer to nominal (104–106%), and no step changes or monotonic trend with accumulated dose was observed, suggesting that the residual high bias likely stems from single-point calibration uncertainty, incomplete warm-up, and sensitivity to pressure and temperature (via the Nernst dependence on pO_2 and T), rather than radiation damage. For deployment in radiation fields without hydrogen, accuracy can likely be improved by enforcing full warm-up, applying in situ pressure and temperature corrections, and performing periodic span checks against a certified standard; concurrent residual gas analyzer (RGA) measurements during these tests validated gas composition and provide a practical path for on-line verification.

The Effect of Hydrogen Gas on the Oxygen Sensor Testing

Because the sensor is expected to encounter hydrogen in service, it was assessed for its cross-sensitivity to H_2. A strong, reversible negative interference that renders readings unreliable even at low H_2 levels was observed. After calibration in air (8.3–8.24 V corresponding to 20.7% O_2, 100–105% recovery by the gas analyzer), exposure to a certified mixture containing 20.0% O_2 and 2.5% H_2 at 50 mL/min and 1,015 mbar drove the indicated O_2 to ~0.1% (0.04–0.09 V), despite the RGA confirming 95–100% recovery for all components; returning to hydrogen-free gas immediately restored correct readings, indicating no permanent loss of sensitivity.

To probe the threshold of the effect, we prepared diluted mixtures by blending a 2.5% H_2 standard with a 9.96% O_2 diluent and verified compositions with a Pfeiffer OmniStar QMG 220. Even at 0.55% H_2 with 12.2% O_2, the sensor reported only ~0.2% O_2, and at 0.15% H_2 with 10.5% O_2 it indicated 3.8% O_2 (36% recovery), while the analyzer confirmed O_2 and H_2 recoveries of ~102–105% and 100%, respectively; in both cases, checks with hydrogen-free standards immediately returned to ~104–105% recovery. The magnitude of the suppression far exceeds the stoichiometric O_2 loss expected from gas-phase reaction (e.g., 0.55% H_2 would consume only 0.275% O_2), implicating processes within the sensor head: the porous platinum electrodes at elevated temperature likely catalyze rapid recombination of O_2 and H_2 to H_2O in the diffusion/pump cavity, collapsing the local oxygen partial pressure that the zirconia cell senses and decoupling it from the bulk stream.

The severity of the bias is therefore governed by catalytic kinetics, diffusion, flow, and sensor temperature rather than the bulk composition alone, making simple stoichiometric correction impractical. Practically, these results show that while the sensor is radiation-tolerant (surviving 14.2 Mrad with only modest drift), it is not suitable for accurate O_2 monitoring in environments where H_2 may be present, even at ≤0.15%. If O_2 measurement is required under such conditions, mitigation would need to precede the sensor and avoid altering O_2 (e.g., by eliminating H_2 generation at the source, relocating the sensor upstream of H_2 ingress, or switching to technologies with minimal H_2 cross-sensitivity such as paramagnetic O_2 analyzers or optical absorption methods); approaches that catalytically "scrub" H_2 will also consume O_2 and thus undermine the measurement.

3.2 HZO IRRADIATIONS

Five HZO samples were irradiated 15 in. from the Van de Graaff accelerator window under a consistent geometry to ensure comparable dose profiles across specimens. Three samples were taken directly from a 0.3 M NaOH slurry; excess liquid was decanted and wicked away, so the solids remained only damp with NaOH during irradiation.

Two additional samples were transferred to an acidic matrix: after removal from NaOH, they were rinsed three times with DI water followed by three rinses with 0.05 M HCl, and excess liquid was again removed so the samples were only damp with the HCl solution. This preparation minimized free liquid, limiting bulk radiolysis while preserving the intended chemical environment for each matrix.

Table 1 summarizes the sample size, matrix, irradiation time, average beam current, and total absorbed dose for all five HZO irradiations.

Table 1. Parameters for five HZO irradiations

Sample Size, g	Solution	Irradiation Time, min	Average Current, uA	Dose, Mrad
1.0572	0.3M NaOH	40	8.56	83
1.1188	0.3M NaOH	80	8.17	150
1.1811	0.3M NaOH	160	8.56	297
1.0989	0.05M HCl	40.5	7.96	75
1.0844	0.05M HCl	80.8	7.20	137

Following exposure, the samples were sent for post-irradiation testing to determine whether dose affected the sorbent's performance in molybdenum (Mo) purification. The test plan includes side-by-side comparisons with unirradiated controls; evaluating uptake capacity, selectivity, kinetics, and column breakthrough/elution behavior, along with supporting materials characterization as needed. These measurements will correlate performance changes with absorbed dose and irradiation matrix and guide process optimization and potential implementation in a commercial production facility.

4 CONCLUSION

The zirconia-based oxygen sensor demonstrated strong radiation tolerance, maintaining functionality and only modest, expected drift after a cumulative dose of 14.2 Mrad, with reproducible responses and percent recoveries of 104–113% against standards. However, hydrogen introduced severe negative interference: 2.5% H_2 drove the indicated O_2 to near zero, and even 0.55% and 0.15% H_2 depressed readings to 0.2% O_2 and 36% recovery, respectively, despite independent verification of gas compositions. The behavior is consistent with catalytic recombination of O_2 and H_2 to H_2O on the porous platinum electrodes, which depletes O_2 prior to detection. Accordingly, while the sensor appears suitable for high-dose environments, its susceptibility to even trace H_2 makes reliable oxygen monitoring in production settings where hydrogen is likely to be present very challenging without additional mitigation, and an alternative O_2 measurement approach may be required.

Five HZO samples were irradiated under a controlled geometry in both alkaline and acidic matrices with minimal free liquid to ensure comparable dose exposure and limit bulk radiolysis. The samples were then submitted for post-irradiation testing against unirradiated controls to determine whether absorbed dose and matrix affect Mo purification metrics. The results will clarify any dose- or matrix-dependent performance changes and guide process optimization and potential implementation in a commercial production setting.

5 ACKNOWLEDGMENT

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