

Control of Volatile Radionuclides from the Dissolution of Used Nuclear Fuel – 10224

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ABSTRACT

Oak Ridge National Laboratory recently completed the head-end portion of the second, coupled end-to-end (CETE) demonstration of advanced nuclear fuel reprocessing to support the Advanced Fuel Cycle Initiative. This research and development (R&D) effort provided a unique opportunity to examine the release of the primary volatile fission and activation products (H-3, C-14, Kr-85, and I-129) contained in used nuclear fuel as well as to evaluate the performance of integrated off-gas treatment systems designed to recover all of these volatile components.

The CETE R&D capability includes all of the processing equipment needed to conduct hot experiments on the primary used nuclear fuel (UNF) processing operations. This begins with the UNF receipt and continues through the production of products and waste forms. The head-end portion includes a voloxidation process step to treat the UNF prior to dissolution. This step oxidizes the fuel and converts it to a free-flowing powder. During this process a major portion of the tritium is released as well as fractions of the other volatile fission products. The preliminary results from the capture of the Kr-85 released during the voloxidation process have already been previously reported. The voloxidized UNF powder, when dissolved, releases much, if not all, of the remaining volatile components to the off-gas stream.

Recently, two batches of the previously voloxidized UNF were dissolved as part of the CETE R&D effort. The off-gas from the dissolution of these kilogram-size batches of UNF flowed through a capture system designed to recover the I-129, C-14, and Kr-85 evolved to determine the fractions released during the dissolution operation. This paper provides the results of these tests.

INTRODUCTION

Oak Ridge National Laboratory (ORNL) has completed the installation of experimental equipment to capture the volatile radionuclides released during the head-end processing of used nuclear fuel (UNF). This work was in support of the Department of Energy Office of Nuclear Energy's Advanced Fuel Cycle Initiative (AFCI) [now called Fuel Cycle R&D (FCR&D)] coupled end-to-end (CETE) research and development (R&D) activity. The new head-end equipment includes a voloxidizer and voloxidation off-gas (VoxOG) capture system, a powder feeder for the dissolver, and a dissolver off-gas (DOG) capture system.

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The head-end processes used in the CETE were located in two separate facilities. The shear and voloxidation equipment was located in ORNL's Irradiated Fuels Examination Laboratory, Building 3525. The dissolution equipment, solvent extraction, and conversion equipment were located approximately 3 miles away in the Radiochemical Engineering Development Center (REDC), Building 7920.

The early release of tritium from the UNF (i.e., before dissolution) is highly desirable as this offers the potential to manage this radionuclide without having to treat the total aqueous inventory of the reprocessing facility. The voloxidation of the UNF has been proposed as a means of releasing a major portion of the tritium (>99%) into the off-gas stream. The voloxidation process also (1) oxidizes the fuel from nominally UO_2 to U_3O_8 ; (2) converts the fuel into a free-flowing powder; (3) releases significant fractions of the other volatile fission products, iodine, C-14 (as CO_2), krypton, and xenon; and (4) separates the fuel powder from the cladding. When the resulting powder is dissolved, much if not all of the remaining volatile components should be released to the DOG stream.

Release limits for reprocessing facilities are specified by a number of regulatory documents, including 40 CFR 190, 10 CFR 20 and 40 CFR 61. These limits are discussed in more detail by Jubin et al. in a previous paper [1]. Current U.S. regulations also require that I-129 and C-14 be sequestered essentially indefinitely. It may however, be possible to manage H-3, xenon, and krypton (e.g., Kr-85) by decay storage.

The experimental integrated off-gas treatment systems were designed to provide the means to recover and to quantify the gases released during the operation of the voloxidation and dissolution processes with the goals of closing the volatile gas material balance around the head-end operations and of determining any interaction between the various volatile gas capture sub-systems. Based on the results of the review of potential processing technologies described above, an initial suite of processes was selected for testing. The proposed capture methods were selected using parameters such as selectivity, efficiency, regeneration of sorbent, and conversion to final waste forms. The initial suite of recovery unit operations included (1) 3A molecular sieves (MS) for tritium recovery, (2) silver-exchanged mordenite (AgZ) for iodine recovery, (3) caustic scrubbing for CO_2 recovery (C-14), and (4) a zeolite (mordenite) (HZ) for absorption of Xe/Kr.

Separate integrated off-gas capture systems have been installed to treat the VoxOG and DOG streams, as these operations are conducted in two separate facilities within ORNL. These systems are identical in capacity and are very similar in regards to the processes used.

A schematic of the head-end off-gas treatment system for the dissolver is shown in Fig. 1. A photograph of the DOG test rack is shown in Fig. 2. The primary differences between the DOG rack and the VoxOG rack are as follows:

1. The VoxOG rack contains a catalytic converter to ensure that all of the tritium is oxidized to tritiated water. The DOG does not contain this operation as it was assumed that virtually all of the tritium contained in the fuel pellets would be liberated in the voloxidizer. (The tritium contained in the cladding [(~40–60%) of the total will be monitored separately and not sent to the dissolver.]

2. The VoxOG rack contains a tritium trap and the DOG rack does not for the same reason as noted for the catalytic converter.
3. The DOG rack contains a NO_x scrubber where the VoxOG rack does not. The source of NO_x is the dissolution of the fuel powder with nitric acid, which will occur only at Building 7920.

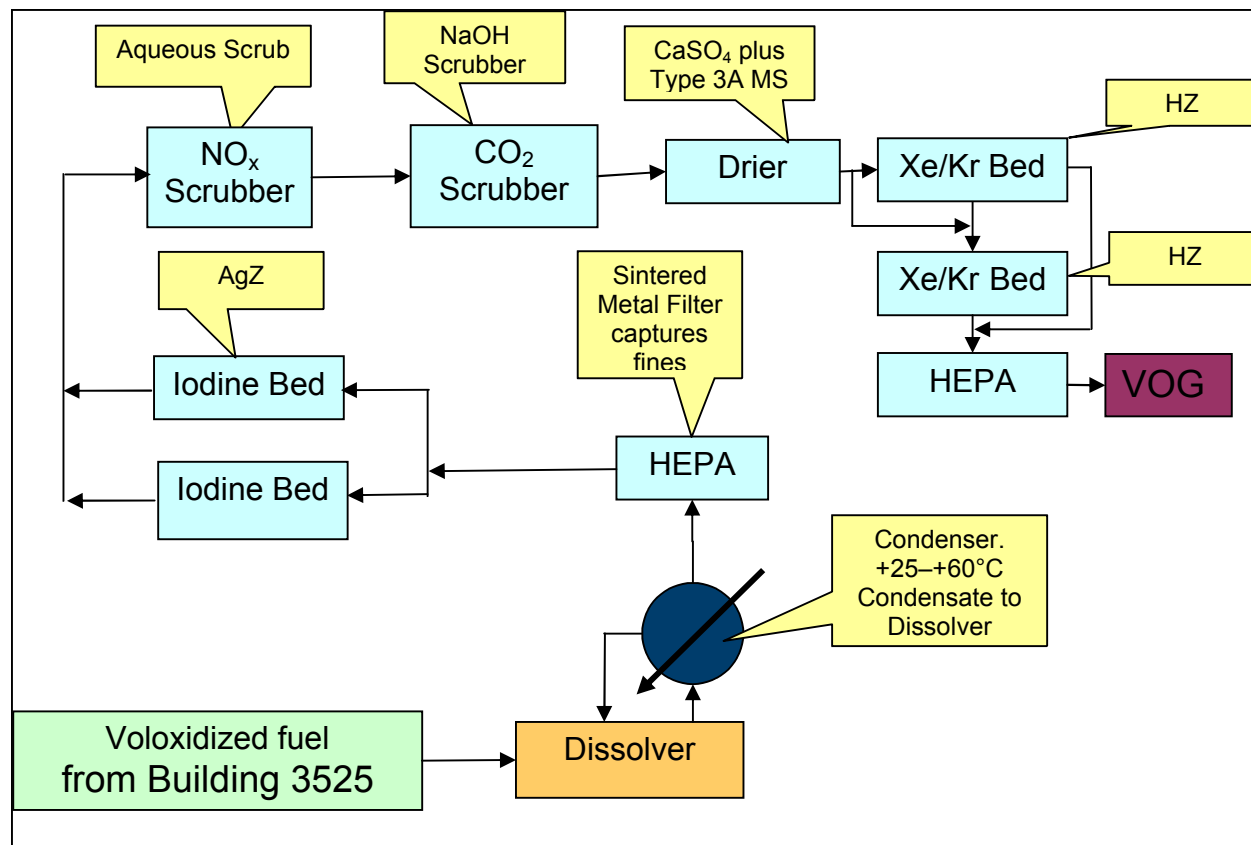


Fig. 1. Dissolver off-gas capture system.

The iodine recovery system is a heated column loaded with two iodine columns each containing five AgZ beds in series. Prior to the installation of the AgZ columns on the rack, the silver on the AgZ is reduced using a 4% hydrogen, 96% nitrogen stream at 200°C. During operation, the iodine traps are heated to ~150°C. Only one column is on line at a time. The first bed is used during the initial dissolution portion of the dissolver run—this is the period of time when the fuel powder is introduced into the dissolver and during the subsequent heat-up of the dissolver to the final operating temperature. The second AgZ column is used during the extended digestion phase of the dissolver operation while the dissolver is heated and sparged. Upon completion of a dissolution operation, the iodine columns are removed from the rack following closure of the block valves. The intact columns containing the five beds are then taken to another facility where the beds are purged with an air stream to remove any physisorbed iodine. The purge gas is passed through a series of liquid bubblers to recover any iodine or tritium that was removed. The beds are then removed from the column for analysis, and the column is reloaded with five beds of the reduced silver mordenite (Ag⁰Z).

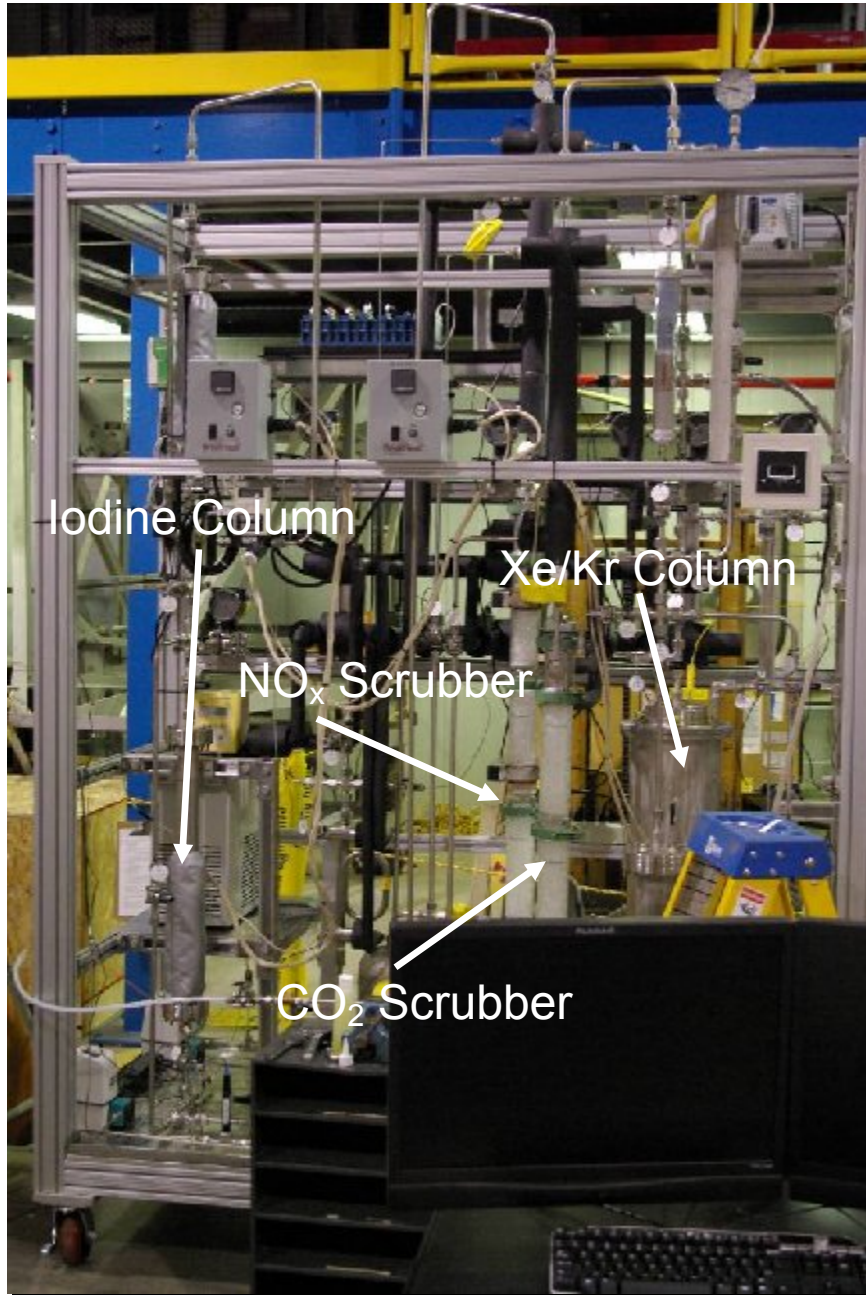


Fig. 2. Dissolver off-gas rack.

The dissolution reactions of the voloxidized fuel result in the production of significant quantities of NO_x . This is removed from the DOG stream by an aqueous scrubber. The gas stream leaving the iodine trap is cooled to ambient temperature and is passed through the NO_x scrubber column. Here the NO_x is removed from the gas stream using water and producing HNO_3 . The scrubber column is packed with glass raschig rings. Upon completion of a dissolution run, the scrubber solution is pumped to a transfer tank, the volume of recovered scrubber solution measured, and a sample pulled and analyzed for tritium, iodine, total carbon, and C-14.

While the bulk of the C-14 found in the irradiated nuclear fuel is assumed to evolve as $^{14}\text{CO}_2$, considerable dilution of the $^{14}\text{CO}_2$ from the dissolver is expected, especially if the sparge gas is not CO_2 -free. In such a case, the DOG $^{14}\text{CO}_2$ will be diluted 1000–5000 times by $^{12}\text{CO}_2$ in the dissolver sparge gas and from inleakage from the cell into the dissolver. The gas stream leaving the NO_x scrubber is routed through the CO_2 scrubber column. Here the CO_2 is removed from the gas stream using 1 N NaOH. The scrubber column is packed with glass raschig rings. Upon completion of a dissolver run, the scrubber solution is pumped to a transfer tank, the volume of recovered scrubber solution measured, and a sample pulled which is and analyzed for tritium, iodine, total carbon, and ^{14}C .

The gas leaving the CO_2 scrubber is then dried using a bank of three drierite and 3A molecular sieves. This is done to remove as much moisture from the gas stream as possible prior to the Kr/Xe trap.

This is the most complex of the recovery systems. The krypton and xenon are trapped using a bed of HZ operated at -80°C . Upon completion of a dissolver run, the trap will be warmed to room temperature, which results in the desorption of a portion of the trapped gases and some segregation of the krypton and xenon occurs. Gases are allowed to expand into an evacuated 50 L expansion tank, where the gas is sampled as is the free volume of the Kr/Xe trap. Then the trap is warmed to $\sim 150^\circ\text{C}$, which desorbs the remaining gases. These gases expand into a second evacuated 50 L expansion tank. This expansion tank and the free volume of the Kr/Xe trap are again sampled, and the gas samples are analyzed to determine the gas composition.

RESULTS AND IMPLICATIONS

The voloxidation tests conducted as part of CETE Run 2 used three separated batches of UNF. The total processing goal was to produce at least 5 kg of UNF to support subsequent R&D. Different operational conditions were used for each voloxidation run to obtain information on reaction properties and the subsequent dissolution properties of product powder (e.g. undissolved solids). The details of the test conditions, batch size, and fuel type are shown in Table I. As the voloxidation tests were carried out, the first two batches of fuel required more than one voloxidation phase to complete. Although not initially planned, the additional phases did provide an opportunity to examine the state of the fuel at an interim point in the oxidation process and provided valuable data.

Table I. CETE Run 2 Used Nuclear Fuel and Test Conditions.

| Batch | Fuel | Burnup (GWd/MT) | Batch Fuel/Total (kg HM/kg) | Segment Length [cm (in.)] | Oxidation Gas | Nominal Temp. ($^\circ\text{C}$) |
|-------|------------|-----------------|-----------------------------|---------------------------|---------------|------------------------------------|
| 1 | Surry-2 | 36 | 1.2/1.7 | 2.54 (1.0) | Air | 500 |
| 2 | North Anna | 63–70 | 2.1/2.9 | 2.23 (0.88) | Air | 600 |
| 3 | North Anna | 63–70 | 2.0/2.8 | 2.23 (0.88) | Oxygen | 600 |

During the course of each voloxidation run and off-gas recovery operation, gas samples were taken between each unit operation at about 1 h intervals. In virtually all cases the subsequent analysis of the 50 cc gas samples for the radionuclides of interest were below the detection

limits. After each run the trapping beds were removed and sampled, the scrubber solution sampled and replaced, the Kr/Xe traps regenerated, and the recovered gas sampled. Table II provides an estimate of the volatile fission and activation products as calculated by ORIGEN for the UNF used in these tests.

Table II. Volatile Fission and Activation Product Estimates Calculated by ORIGEN.

| | Fuel Source | | | |
|-----------------|--------------------|----------------------------|--------------------|----------------------------|
| | Surry | | North Anna | |
| | Grams per MTIHM | Bq (Ci) per MTIHM | Grams per MTIHM | Bq (Ci) per MTIHM |
| Krypton | | | | |
| Kr-82 | 0.60 | | 2.05 | |
| Kr-83 | 35.61 | | 61.00 | |
| Kr-84 | 136.22 | | 228.00 | |
| Kr-85 | 4.73 | 6.85E+13 (1852.80) | 31.70 | 4.62E+14 (12500.00) |
| Kr-86 | 199.30 | | 329.00 | |
| Kr Total | 376.46 | 6.85E+13 (1852.80) | 651.75 | 4.62E+14 (12500.00) |
| Xenon | | | | |
| Xe-128 | 2.38 | | 12.00 | |
| Xe-130 | 8.94 | | 24.90 | |
| Xe-131 | 525.62 | | 627.00 | |
| Xe-132 | 1121.31 | | 2479.00 | |
| Xe-134 | 1660.07 | | 3050.00 | |
| Xe-136 | 2558.00 | | 4680.00 | |
| Xe Total | 5876.31 | | 10872.90 | |
| Carbon | | | | |
| C-12 | 4.64E-04 | | 6.78E-04 | |
| C-13 | 1.40E+01 | | | |
| C-14 | 3.16E-03 | 5.22E+08 (1.41E-02) | 6.15E-03 | 1.01E+09 (2.74E-02) |
| C Total | 1.40E+01 | 5.22E+08 (1.41E-02) | 6.83E-03 | 1.01E+09 (2.74E-02) |
| Iodine | | | | |
| I-127 | 49.93 | | 94.30 | |
| I-129 | 162.06 | 1.06E+09 (2.86E-02) | 318.00 | 2.07E+09 (5.61E-02) |
| I Total | 212.00 | 1.06E+09 (2.86E-02) | 412.30 | 2.07E+09 (5.61E-02) |
| Tritium | | | | |
| H-1 | 7.80E-03 | | 1.15E-02 | |
| H-2 | 4.00E-03 | | 5.36E-03 | |
| H-3 | 1.41E-02 | 5.03E+12 (1.36E+02) | 9.69E-02 | 3.47E+13 (9.37E+02) |
| H Total | 2.59E-02 | 5.03E+12(1.36E+02) | 1.14E-01 | 3.47E+13 (9.37E+02) |

The first batch of material tested under CETE used Surry-2 fuel with an initial enrichment of 3.11% and a burnup of 36 GWd/MT heavy metal. The cooling time was 27 years (the fuel was discharged from the reactor in 1981). The amount of material tested was 1704 g (316 g hulls and 1388 g of fuel). The fuel was oxidized in air at about 500°C. The run was prematurely terminated due to apparent cessation of oxygen consumption that occurred after 4 h of operation at temperature. Inspection of the fuel product powder and hulls showed that the fuel was only ~70% oxidized. Following inspection of the residual fuel, the complete batch was rerun under the same conditions. Operation continued at temperature for 4 h to ensure complete oxidation.

The second batch of fuel processed in voloxidation was ~2.4 kg of North Anna used fuel with an initial enrichment of 4.199% and a burnup of 63–70 GWd/MT heavy metal. A total of 2.9 kg of fuel and hulls were used. The feed gas for this batch was air, and the nominal operating temperature was 600°C. For a variety of reasons, the second batch of fuel ultimately required three separate voloxidation operations. The first phase was terminated when the krypton breakthrough of the krypton bed was observed. The second portion of the run was terminated when an anomaly in the oxygen consumption was observed; the anomaly was later attributed to the gas feed tube coming loose in the voloxidizer, which allowed the gas to bypass the fuel. Following the reattachment of the gas feed tube, a third run was completed on the partially voloxidized fuel. Oxygen consumption and krypton release decreased as fuel was completely oxidized, as expected, and no breakthrough of the krypton trap was observed.

The third batch of material was the same as that used in the second test. Approximately 2.3 kg of fuel and hulls was used. This test was conducted using an oxygen atmosphere rather than air. The fuel was oxidized at about 600°C. Due to the anticipated inleakage around the rotary seals, some nitrogen was present in the voloxidizer. This inleakage also meant that there was always a small flow of nitrogen in addition to residual oxygen to carry the off-gas to the off-gas treatment system. Krypton release decreased as fuel was completely oxidized, as expected, and no breakthrough of the krypton trap was observed. Post-run physical observation of the fuel showed complete removal of the fuel from the cladding and the anticipated fine fuel powder.

Table III summarizes the krypton released and recovered during the voloxidation operations.

Table III. Summary of the Krypton Recovered During the Voloxidation Operations.

| Fuel, Oxidation Phase # | Fuel (g-HM) | ORIGEN Estimate Initial [Bq (Ci)] | Recovered from Off-gas Traps [Bq (Ci)] | Released by Volox (%) |
|-------------------------|-------------|-----------------------------------|--|-----------------------|
| Surry-2, Phase 1 | 1223 | 8.36E+10 (2.26) | 8.44E+09 (0.228) | 10.0 |
| Surry-2, Phase 2 | | | 2.67E+09 (0.0723) | 3.3 |
| TOTAL | | | | 13.3 |
| North Anna, Phase 1 | 2071 | 9.58E+11 (25.9) | ~4.07E+11 (~11.) est | ~42. (est) |
| North Anna, Phase 2 | | | 5.59E+10 (1.51) | 5.6 |
| North Anna, Phase 3 | | | 1.68E+11 (4.53) | 16.9 |
| TOTAL | | | | 64.5 |
| North Anna, Phase 1 | 2012 | 9.32E+11(25.2) | 4.96E+11 (13.4) | 53.2 |
| TOTAL | | | | 53.2 |

Analysis of trapping media for iodine indicates that during the voloxidation operations, very little iodine was released and recovered. All of the iodine recovered was found in the catalyst bed and tritium trap. No iodine was detected in either the downstream iodine traps or the CO₂ scrubber caustic solution. Based on comparisons with ORIGEN predictions of the fuel composition, iodine releases ranged from ~0.04% to ~0.13%. The release/recovery is lower than the 1% removals estimated from the literature.

Analysis of the CO₂ scrubber solutions indicated that $\sim 1.11 \times 10^7$ Bq ($\sim 3 \times 10^{-4}$ Ci) of C-14 per kilogram of fuel voloxidized (heavy metal basis) was released to the off-gas and recovered. This is ~10 times more C-14 recovered than was estimated by our initial ORIGEN calculations to be present in the fuel. We believe that the difference may be accounted for because the ORIGEN calculations did not initially include certain contaminants (e.g., N-14) in the initial as-fabricated fuel composition. We are currently attempting to obtain the actual impurity levels in the as-fabricated fuel. The anticipated C-14 levels can be bounded by examining the fuel specifications and rerunning ORIGEN at these conditions. Table IV shows the quantities of C-14 predicted in the North Anna fuel at various N-14 impurity levels.

Table IV. Impact of ORIGEN Calculated C-14 in UNF as a Function of N-14 Impurities.

| Assumptions of N-14 Impurity Level in Fresh Fuel | g C-14/MT Fuel |
|--|----------------|
| None present | 0.00615 |
| 35 ppm | 0.375 |
| 75 ppm (ASTM limit) | 0.8 |

If one assumes that all of the C-14 was released during voloxidation, then the quantity recovered in the CO₂ scrubber equates to 0.085 g/MT or to an estimated initial N-14 impurity level of ~8 ppm, which is well within the ASTM specification.

Following voloxidation, the U₃O₈ fuel powder and hulls were sent to the REDC facility for dissolution. The purpose of the fuel dissolution step is to prepare the solid fuel for subsequent liquid separations steps. This is accomplished by dissolving the fuel solids into concentrated nitric acid. During the dissolution process, additional gases are evolved. Oxides of nitrogen are the primary off-gas components generated by the reactions of nitric acid and the fuel oxides; however, during the dissolution and sparging of the resulting solution, iodine, C-14 as carbon dioxide, xenon, and krypton gasses are also released to the off-gas stream. Portions of each of the two North Anna voloxidation batches of fuel powder were dissolved separately to allow the collection of the data to complete the volatile gas material balances and to allow the determination of the impacts of the variations in fuel type and voloxidation conditions.

The first dissolution run utilized 1180 g of the U₃O₈ powder from the North Anna fuel that had been voloxidized in air at 600°C. Hulls were separated prior to dissolution. The dissolver was charged with 8 M nitric acid and heated to 40°C. The fuel powder was loaded in a feed hopper installed on the dissolver. The powder feeder allowed small quantities of powder to be introduced into the dissolver in discrete ~150 to 200 g batches. In this run the feed was introduced over a ~30 min period. During this time the evolution of krypton was monitored using the in-line gamma monitor on the off-gas line leading to the DOG rack. Following the initial

30 min dissolution phase, the feed hopper was flushed with acid and the heating of the dissolver to 90°C was initiated. When the dissolver reached the 90°C digestion temperature, the initial iodine trap was valved out and the second trap placed in service. The digestion continued over an 8 h period. The resulting dissolver solution was filtered to recover any undissolved solids for later analysis.

The second dissolution run was very similar in nature; 1180 g of U_3O_8 from the North Anna fuel that was voloxidized in oxygen was processed. In this case the fuel was introduced via the powder feeder over a 60 min period. As in the previous case, the iodine evolved during the dissolution and digestion phases was captured separately, as during the initial dissolver run.

Surry fuel was not processed.

The real-time gamma monitoring results for the krypton evolution during first dissolution run are shown in Fig. 3. The dissolution process started at 14:26 when the first batch of fuel was added to the dissolver. At 14:27 Kr-85 was first detected by the gamma monitor on the off-gas line leading to the DOG rack. Over the next 17 min five additional batches of fuel were introduced. At 14:52 a 2.54 cm (1 in.) steel plate was placed between the off-gas line and the gamma monitor to reduce the dead time in the detector. At ~15:09 the acid flush of the fed powder was completed. At 15:30 the initial iodine trap was valved out, the second trap was placed on line, and the heating of the dissolver to 90°C was initiated. Digestion temperature was reached at 16:47. At 15:27 the steel plate was removed as the Kr-85 activity in the DOG was significantly reduced. At 16:01 Kr-85 was detected in the off-gas line, and at 16:14 the second krypton trap was placed on line. At 18:04 the krypton trapping operation was terminated. The bulk of the krypton appears to have been released during the first 60 min of the dissolution operation.

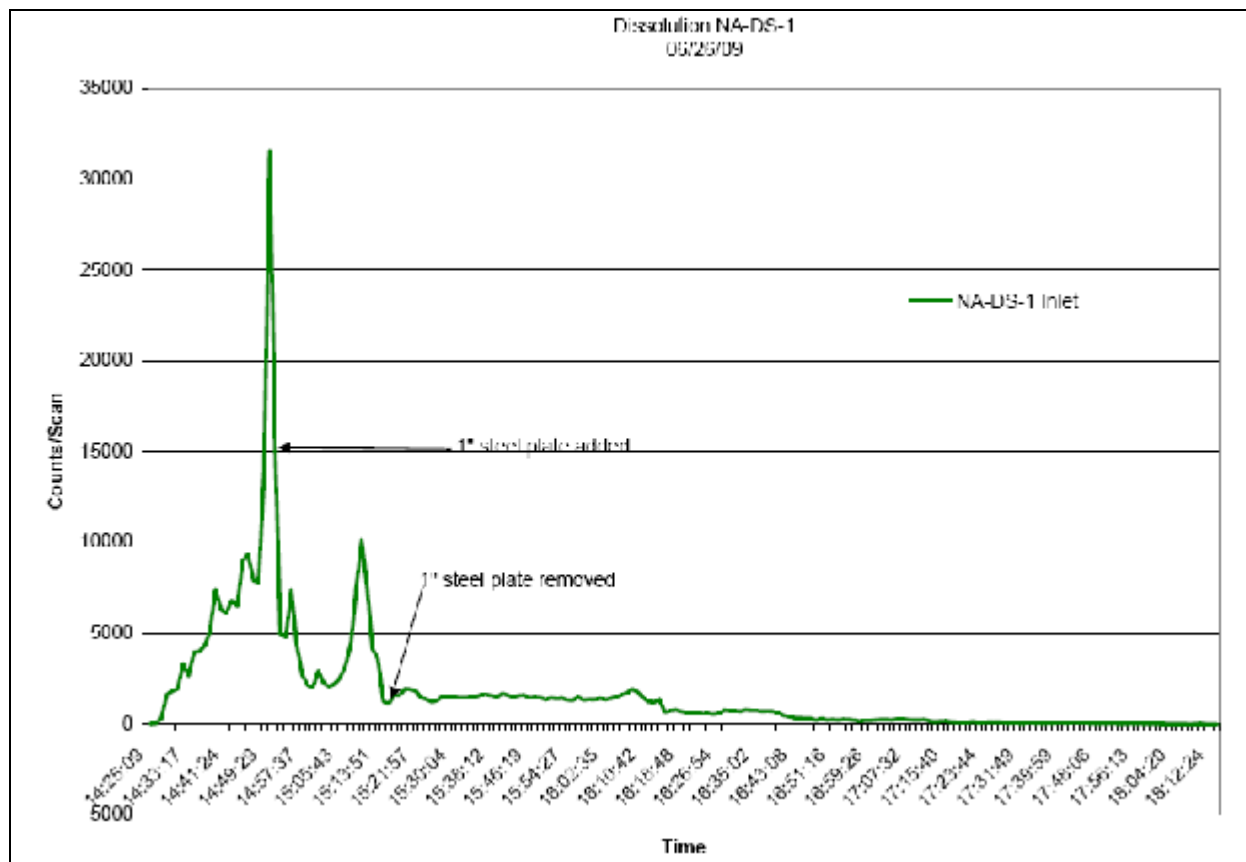


Fig. 3. Real-time Kr-85 gamma scan of the DOG off-gas line.

Following each of the two runs, the iodine traps were removed, the NO_x and CO₂ scrubber solutions were sampled and the Kr/Xe beds were regenerated.

Good agreement was achieved between the online gamma monitors on the DOG line, the gamma scan of the loaded Kr/Xe bed, and samples taken from the gas expansion tanks during the post-run Kr/Xe recovery operations. The comparisons are shown in Table V. Also shown on this table are the krypton recovery percentages from the voloxidation operations. Note that the total krypton recovered ranges from ~105% to 120% of the amount calculated by ORIGEN. The analytical uncertainty in the rare gas analysis (RGA) is ±10% for signals >5 times background and ±20% for signals <5 times background, so this range is within the error of that analytical technique.

Table V. Krypton Recovery During Dissolution and Voloxidation Operations Using North Anna Fuel

| | Fuel Oxide (g) | ORIGEN Estimate Initial [Bq (Ci)] | Gamma Scan Inlet [Bq (Ci)] | Gamma Scan Trap [Bq (Ci)] | Trap Loading Based on Desorption Gas Analysis [Bq (Ci)] | Recovered vs ORIGEN Estimate (%) |
|--|----------------|-----------------------------------|----------------------------|---------------------------|---|----------------------------------|
| North Anna— Air Voloxidation | | | | | | |
| Dissolution | 1180 | 4.44E+11 (12) | 1.45E+11 (3.93) | 1.29E+11 (3.49) | 1.77E+11 (4.78) | 39.8 |
| Voloxidation | | | | | | ~65 |
| North Anna— O ₂ Voloxidation | | | | | | |
| Dissolution | 1180 | 4.44E+11 (12) | 2.87E+11 (7.75) | 2.98E+11 (8.06) | Pending | 67.0 |
| Voloxidation | | | | | | 53 |

Upon completion of a dissolution run, the iodine traps were removed from the rack following closure of the block valves located at each end of the column. The intact columns containing the five beds were then taken to another facility, where the beds were purged with an air stream to remove any physisorbed iodine. The purge gas was passed through a series of liquid bubblers to recover any iodine or tritium that was removed. The individual AgZ beds were then removed from the column for analysis and the column was reloaded with five beds of Ag^oZ for reuse in the next dissolver run.

Trace quantities of tritium (~0.03% of estimated total) were recovered during the purging of the iodine traps from the first North Anna fuel dissolution. No tritium was detected in any of the other samples from the DOG system. The fraction remaining in the dissolver solution is still pending.

Overall there was good agreement on total iodine recovered from two dissolution operations. The total quantities of I-129 recovered were 9.84×10^5 Bq (2.66×10^{-5} Ci) and 1.12×10^6 Bq (3.02×10^{-5} Ci) for the first and second dissolver operations, respectively. These totals account for about ~50% of the I-129 predicted in the ORIGEN calculations. The analyses of the iodine beds indicated that the major fraction (65–94%) of the iodine released during the 9 h dissolution operation occurred during the digestion phase of dissolver run. At the time of this writing, analysis to determine the fraction of iodine remaining in the dissolver solution is still pending.

The total amount of C-14 recovered in the NO_x and CO₂ scrubber solutions were 1.18×10^7 Bq (3.2×10^{-4} Ci) and 8.40×10^6 Bq (2.27×10^{-4} Ci) for the first and second dissolver operations, respectively. These results are summarized in Table VI.

Table VI. C-14 Recovery from the Dissolution of the North Anna Fuel

| | Dissolver Run 1 [Bq (Ci)] | Dissolver Run 2 [Bq (Ci)] |
|---|------------------------------|------------------------------|
| ¹⁴ C recovered in NO _x scrubber | 3.85E+06 (1.04E-04) | 0 (0) |
| ¹⁴ C recovered in CO ₂ scrubber | 7.99E+06 (2.16E-04) | 8.40E+06 (2.27E-04) |
| Total ¹⁴ C recovered | 1.18E+07 (3.20E-04) | 8.40E+06 (2.27E-04) |

Based on the mass of fuel dissolved in each run, this amounts to 8.40×10^6 Bq (2.27×10^{-4} Ci) to 1.18×10^7 Bq (3.20×10^{-4} Ci) per kilogram of heavy metal. These values are virtually the same as observed during the voloxidation operations on a heavy metal basis. Again, this is ~10 times more C-14 recovered than estimated present in the fuel and indicates a 50/50 split in C-14 releases from the voloxidation and dissolution processes used. Based on the total C-14 recovered, a total of 0.17 mg C-14 was released per kilogram of heavy metal, which would be indicative of a N-14 impurity level of ~16 ppm.

SUMMARY

Integrated off-gas capture systems have been installed to quantify the volatile gases released during the voloxidation and dissolution of UNF. During FY 2009, three batches of light water reactor fuel were voloxidized at various conditions in batch sizes ranging from ~1 kg to ~2 kg each. The total amount of fuel processed was ~5.3 kg on a heavy metal basis. The fuel used was from two different reactors with burn-ups from 34 to 72 GWd/MT. Excellent correlation between the observed reactions in the voloxidizer and the release of krypton to the off-gas system has been noted. A large fraction (nearly 100%) of the tritium was released from the fuel during voloxidation. This does not include the tritium contained in the cladding. Analysis of the cladding is still pending. About 40–50% of the krypton was released from the North Anna fuel during the voloxidation step. This is significantly more than the 5–10% reported in the literature. Less than 1% of the iodine was released during voloxidation.

Approximately 2 kg of the voloxidized fuel was then dissolved in two batches. About 40–65% of the total calculated krypton was recovered from the DOG. Total Kr-85 is slightly above 100% of the amount calculated by ORIGEN. Carbon-14 release fractions from dissolution and voloxidation operations are approximately the same. This is similar to literature reported values of 50% release during voloxidation. The bulk of the iodine releases occurred during the digestion phase of the dissolution process. The total I-129 recovered is about half the amount expected. Further analysis of feed materials and dissolver solutions continues to confirm the fraction of iodine release and capture.

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