Analysis of F-Canyon Effluents During the Dissolution Cycle with a Fourier Transform Infrared Spectrometer/Multipath Cell

by

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Abstract	1
Introduction	1
Experimental	1
Discussion and Results	4
Conclusion	10

List of Tables

Table 1.	Decladding and dissolution process in conjunction with air bag collection sequence	2
Table 2.	Chemicals and their respective vibrational frequencies	4
Table 3.	Air sample concentration analysis (ppm). Kr-85 is in dpm/cc of air.	8

List of Figures

Figure 1.	FTIR spectrometer/multipath cell assembly	11
Figure 2.	Absorption spectrum of WA7 Sample	12
Figure 3a and 3b.	Infrared absorption spectra of WA7 sample with spectroscopically removed and with background subtraction (WA5)	12
Figure 3c.	Amplification of small infrared absorption bands in Figure 3b	13
Figure 4.	Simplified schematic of F-Canyon stack	13
Figure 5.	Infrared absorption of spectra of NO ₂ , NO, N ₂ O, and HNO ₂	14
Figure 6.	Three-dimensional plot (intensity-wavenumber-time)	14
Figure 7.	Concentration plot v. time. Kr-85 data is in disintegrations per minute per ml of air (dpm/cc)	15
Figure 8.	Passive spectrum of ammonia (plume-sky) and library sequence	16

Abstract

Air samples from F-Canyon effluents were collected at the F-Canyon stack and transported to a laboratory at the Savannah River Technology Center (SRTC) for analysis using a Fourier transform infrared spectrometer in conjunction with a multipath cell. Air samples were collected during the decladding and acid dissolution of the irradiated aluminum-cladded slugs. The FTIR analyses of the air samples show the presence of NO_2 , NO , HNO_2 , and N_2O during the dissolution cycle. Also SF_6 that was inserted in the stack annulus as part of a tracer experiment was observed in the stack. The concentration time profiles of these effluents corresponded with expected release rates from the F-Canyon operations and correlated with measurements of ^{85}Kr made on the same air samples.

Introduction

F-Canyon restart offers a unique opportunity to identify organic and inorganic effluent signatures not previously studied and concentration profiles associated with the processes. The restart also offers the opportunity to develop nonproliferation technologies and methodologies to identify the gaseous effluents released to the atmosphere. F Canyon at the Savannah River Site (SRS) started processing irradiated aluminum-cladded uranium slugs on February 13, 1997. Since access to the stack was not possible before the November 3-8, 1996 dissolution, previous studies were conducted using a tethered balloon equipped with an air sampler for laboratory analysis and a Fourier transform infrared spectrometer operating in the passive mode.

The waste stabilization process on irradiated aluminum-cladded uranium slugs is similar to fuel reprocessing. The dissolution process occurs in three phases. In the first phase, the aluminum cladding is removed from the slugs with a 50-50% NaNO_3 and NaOH solution. Ammonia produced during the decladding process is released through one of the dissolver stacks attached to the main stack. The decladding phase is followed by the dissolution of the uranium slugs using HNO_3 . In this phase, large quantities of NO_x are released to the stack. NO and NO_2 are the major contributors in the gaseous plume. The third phase consists of extracting plutonium using tributyl phosphate (TBP) diluted in n-paraffin. Several hydrocarbons are expected to be released to the atmosphere during this phase.

During the past several years, improvements were made to the canyons to reduce NO_x emissions. Previous dissolution of targets (prior 1990) were clearly identified by the brown plume emanating from the canyon stack. In contrast, present-day dissolutions are vaguely identifiable by a light brown haze over the stack. The weak appearance of the plume is the result of changes in operating procedures, modifications to the scrubbers, and the addition of ventilation fans.

Access to the main stack was available for dissolution #9. Dissolution #9 occurred during the week of November 3-8, 1996. The air samples extracted from the main stack provided the first glimpse of the inorganic effluents released to the atmosphere during the decladding and dissolution cycles.

Experimental

During the week of November 3-8, 1996, the Nonproliferation Technologies Section was able to install a temporary air sampler in the main stack with multifunctional capabilities. One of the capabilities of the air sampler was to fill 5-liter Tedlar™ bags for analysis in the laboratory. The air bags were collected at predetermined times during the decladding and dissolution cycles.

F-Canyon personnel loaded the canyon with a 22 "bucket" charge corresponding to 14.7 metric ton units (MTU). Charge #9 data is shown in Table 1 in conjunction with the air collection sequence (WA# stands for Whole Air #).

Table 1. Decladding and dissolution process in conjunction with air bag collection sequence

Process	Time	Date	Time Collected	Day Collected
Coating Removal Started	0348	11/04/96		
WA1			0800	11/4/96
WA2			0820	11/4/96
WA3			1300	11/4/96
WA4			2345	11/4/96
WA5			0745	11/5/96
Coating Removal Ended	2230	11/05/96		
1st Acid Cut Started (began heating)	0910	11/06/96		
WA6_A&B			1200	11/6/96
1st Cut at 95C	1300	11/06/96		
WA7_A&B			1400	11/6/96
WA8			1600	11/6/96
1st Acid Ended	1943	11/06/96		
WA9			2400	11/6/96
WA10			0800	11/7/96
2nd Acid Cut Started (began heating)	1304	11/07/96		
WA11			1600	11/7/96
2nd Cut at 95C	1730	11/07/96		
WA12			1800	11/7/96
WA13			2000	11/7/96
WA14			2400	11/7/96
2nd Cut Ended	0001	11/08/96		
WA15			0800	11/8/96

The air samples were delivered to an Nonproliferation Technologies Section (NTS) laboratory at SRTC immediately after collection. The air samples were admitted to a 9.8-meter multipath cell for the analysis using a Fourier transform infrared spectrometer. In most cases, the samples were analyzed approximately two hours after collection. The air samples were analyzed using a Fourier transform infrared spectrometer manufactured by Midac Corporation. The illuminator (Michelson interferometer box) was assembled in an enclosure

containing a 9.8-meter multipath cell, gold-coated mirrors, and a mercury cadmium telluride (MCT) detector as shown in Figure 1. The interferometer and the multipath cell were equipped with ZnSe optics (beam splitter and windows). The interferometer was warmed for a minimum period of eight hours before the sample analysis to ensure stability. Interferograms were recorded at 0.5 and 2 cm^{-1} resolutions and converted to single-beam spectra using triangular apodization. A total of 2048 samples were co-added for the 0.5 cm^{-1} resolution spectra. A total of 512 scans were co-added for the 2 cm^{-1} resolution spectra. A zero fill of 2 was used in the single-beam spectra prior to mathematical manipulations. Background interferogram spectra were also recorded at 0.5 and 2 cm^{-1} resolutions with an evacuated cell (2 torr) to obtain the instrument response.

Prior to the air sample analysis, the cell was evacuated with a mechanical pump and flushed several times with dry nitrogen. Approximately 3 liters of the 5-liter TedlarTM bag was admitted into the evacuated multipath cell. Samples were analyzed in a period of time up to 3 hours. The period of time was determined by the number of co-added scans (512, 1024, 2048) and the resolution (0.5 cm^{-1} , 2 cm^{-1}) during the data acquisition. Absorbance spectra of the air samples were obtained by using single beam spectra of the sample and the background (evacuated cell). Figure 2 shows a typical absorbance spectrum (WA7).

To identify other spectral features belonging to other compounds, water was spectroscopically removed from the spectra using the wet nitrogen method. In this method, the air sample absorption spectrum is used as a background in real time data acquisition. Nitrogen is bubbled through water and directed to the cell. At the right concentration, most of the water lines are eliminated from the absorption spectrum. At this point, the water spectrum is recorded and used as water reference spectrum for other spectra. Figure 3a shows the absorbance spectrum of WA7 without the water. It is evident in Figure 3a that the absorption bands belonging to NO and HNO₂ were previously obscured by the water absorption bands. Further spectral improvement was obtained by subtracting the canyon air background in air sample WA5 as shown in Figure 3b.

During the collection of air samples, the Aerospace group conducted plume imaging experiments by releasing SF₆ gas into the annulus of the stack. In these experiments, SF₆ gas released in the annulus mixed with the stack air at the top of the stack (approximately 200 ft). The air sample collection port of the stack is located approximately 100 feet above ground. Several absorbance spectra have the SF₆ "fingerprint" located at 947 cm^{-1} . The spectra containing SF₆ coincide with the introduction of SF₆ into the annulus by the Aerospace group. This result lead to the hypothesis that a leak occurred between the annulus and the main stack where the sampling port is located. This condition was later confirmed with engineers familiar with the stack design and modification history. Figure 4 shows a simplified schematic of the F-Canyon stack.

The infrared spectra were analyzed for a variety of chemicals, which included NO₂, NO, N₂O₅, N₂O₄, HNO₃, HNO₂, N₂O, and NH₃. Only NO₂, NO, N₂O, HNO₂, and SF₆ were clearly identified in the spectra, and their concentrations were quantified using digitized spectra from Infrared Analysis, Inc. Other weak infrared absorption bands were found superimposed on the HNO₂ absorption bands at 826 and 808 cm^{-1} . Another spectral feature above the noise level was found at 1718 cm^{-1} . It is not clear the origin of these bands. NO₂ has two major absorption bands located at 2907 and 1617 cm^{-1} . The band at 1617 cm^{-1} is superimposed in a water absorption band and is easily optically saturated at large NO₂ concentrations. At large NO₂ concentrations, the quantification process was performed using the 2907 cm^{-1} band. Table 2 shows the vibrational frequencies for the chemical of interests.

Table 2. Chemicals and their respective vibrational frequencies

Chemical	Vibrational Frequency (cm ⁻¹)	Detection
NO ₂	2907, 1617	Yes
NO	1876	Yes
N ₂ O	2224	Yes
HNO ₃	895, 885, 879	No
HNO ₂	1254, 853, 791	Yes
N ₂ O ₄	1261, 750	No
N ₂ O ₅	1245, 743	No
NH ₃	966, 931	No
SF ₆	947	Yes

Air samples were analyzed for ⁸⁵Kr content by J. R. Cadieux from the Environmental Chemistry Group of Nonproliferation Technologies Section (NTS). F-Canyon stack samples were analyzed by liquid scintillation counting (LSC). A 1.0-ml aliquot of air was removed from each F-Canyon stack gas sample by disposable syringe. The aliquot was transferred to a 25-ml glass LSC vial containing 22 ml of Ultima Gold Extended Range scintillation cocktail through a Teflon-coated, silicone-rubber septum. The head space above the cocktail was evacuated, and the air sample slowly bubbled into the cocktail over a period of 2-3 minutes. The vial was inverted and shaken for several minutes to disperse the air in the cocktail. A 1.0-ml aliquot of an ⁸⁵Kr standard demonstrated that the uptake of the activity in the cocktail was quantitative to within plus or minus 5%. A reagent blank was prepared with laboratory air. LSC measurements were made on a Packard TR2500 counter.

Individual samples and a background (lab air injected into cocktail) were measured for 60 minutes each with counting statistics ranging from 2 to 4% (two sigma). The counts per minute (cpm) are for a window from 0 to 700 keV. The counting efficiency for this energy beta was estimated to be greater than 90%. The quench correction was based on Packard's transformed spectral index of an external Ba-133 standard (tSIE). Sample WA6A was prepared in quadruplicate, and the replicates were counted repeatedly to give counting statistics of 0.3 to 0.4% (two sigma). Repeated measurements of one of these replicates of a period of a week showed no decrease in counting rate. The average net value was 110 cpm with an RSD of 4 cpm. Samples WA13, WA14, and WA15 were reprocessed, and the net activity in WA14 was reproducible and well above counting statistics. Table 3 shows the ⁸⁵Kr data in disintegrations per minute per cc of air (dpm/cc).

Discussion and Results

The Savannah River Site submitted reports to the South Carolina Health Department of Health and Environmental Control (SCDHEC) that accounts for all chemical releases to the atmosphere from SRS operations. Since the concentrations for many of these chemicals were never measured, an annual estimate was prepared to satisfy the South Carolina law. Several assumptions in the calculations were made to report

the maximum total annual production of ammonia and NO_x for the continuous dissolution of targets. The assumption was made that the dissolver is loaded with 15 metric tons units of MK31A (uranium targets). The cladding removal is approximately completed in 21 hours. The cycle process begins by the removal of the aluminum coating according to the chemical reaction shown below.

The primary effluents resulting from the decladding process are ammonia and hydrogen. At the F Canyon, the NH₃ is released through one of the two 6-inch diameter stainless steel dissolver stacks. The two dissolver stacks run up the outside of the main stack.

The emission of NH₃ per 15 MTU run released to the air is calculated as follows. It is known that 15 MTU contains 856 lb of aluminum. The November 3-8 dissolution was 14.7 MTU.

$$Total_NH_3 = \left(\frac{856_lb_Al}{15_MTU} \right) \times \left(\frac{14.7_MTU}{run} \right) \times \left(\frac{0.454_kg}{lb} \right) \times \left(\frac{1_mol_Al}{27_g_Al} \right) \times \left(\frac{03_mol_NH_3}{1_mol_Al} \right) \times \left(\frac{17_g_NH_3}{1_mol_NH_3} \right)$$

$$Total_NH_3 = \frac{719_kg_NH_3}{run}$$

F-Canyon personnel estimated that approximately 240 cfm of air from the dissolver mixes with approximately 900 lb of steam per hour in the dissolver stack. Assuming water vapor at 100 degrees C and using the ideal gas law, the total water vapor volume released to the stack is approximately 6.95×10^5 liters per hour or the equivalent to 409 cfm (water condensation was not taken into account in this calculation). Therefore, the total flow through the dissolver stack is approximately 650 cfm. The decladding process occurs in a period of approximately 21 hours. The total production of ammonia during the run is shown below.

$$Total_NH_3 = \left(\frac{719_kg}{run} \right) \times \left(\frac{10^6_mg}{kg} \right) \times \left(\frac{1_run}{21_hr} \right) \times \left(\frac{1_hr}{60_min} \right) \times \left(\frac{1_min}{650_ft^3} \right) \times \left(\frac{1_ft^3}{0.0283_m^3} \right)$$

$$Total_NH_3 \approx 3.1 \times 10^3 \frac{mg}{m^3}$$

$$Total_NH_3 = \frac{3.1 \times 10^3 \times 24.45}{17} \approx 4.5 \times 10^3 \text{ ppm}$$

Therefore, for the decladding process of a 14.7 MTU charge, and a time period of 21 hours, a concentration of approximately 4.5×10^3 ppm was released to the air.

The aluminum cladding removal is followed by the dissolution of the uranium slugs with nitric acid. The uranium slugs are dissolved in a two-step process called the first and second acid cuts. Uranium is dissolved according to the reaction shown below with the production of NO and NO₂.

Further, it is assumed that NO is readily converted to NO₂ in the presence of air as follows:

14.7 MTU is associated with a minimum of 778 lb (353 kg) of aluminum. Therefore, the amount of uranium dissolved is 14.35 MT of uranium. The total amount of NO_x produced from the uranium is:

$$\frac{\text{Maximum_NO}_2\text{-evolution_ (kg)}}{\text{run}} = \left(\frac{14.35_MTU}{\text{run}} \right) \times \left(\frac{1000_kg}{MTU} \right) \times$$

$$\left(\frac{1.0_mol_U}{0.238_kg_U} \right) \times \left(\frac{2.42_mol_NO_2}{1_mol_U} \right) \times \left(\frac{0.046_kg_NO_2}{1_mol_NO_2} \right)$$

$$= \frac{6.7 \times 10^3 \text{ kg_NO}_2}{\text{run}}$$

Therefore, 6.7×10^3 kg of NO_x were produced during the dissolution of 14.35 metric tons of uranium in a charge of 14.7 MTU. The dissolving phase of the uranium fuel was generally completed within 22 hours. The first and second acid cuts in the dissolution process used to run back to back with little time between them. Dissolution #9 shows a large time gap between the acid cuts. The process nowadays last approximately 48 hours. The air flow through the canyon stack is estimated at 240,000 cfm. For calculation purposes, assume a constant source of NO_x for 48 hours. Therefore, the total NO_x released to the air in mg/m³ for 14.35 metric tons of uranium dissolved in a period of 48 hours with a flow rate of 240,000 cfm is shown below.

$$\text{Total_NO}_x = \left(\frac{6.7 \times 10^9 \text{ mg_NO}_x}{\text{run}} \right) \times \left(\frac{1_run}{48_hr} \right) \times \left(\frac{1_hr}{60_min} \right) \times \left(\frac{1_min}{240,000_ft^3} \right) \times \left(\frac{1_ft^3}{0.0283_m^3} \right)$$

$$\text{Total_NO}_x = \frac{3.4 \times 10^2 \text{ mg}}{m^3}$$

$$\text{Total_NO}_x (\text{ppm}) = \frac{3.4 \times 10^2 \frac{\text{mg}}{m^3} \times 24.45}{46}$$

$$\text{Total_NO}_2 = 180 \text{ ppm}$$

Sample data of dissolver acid cut solutions show that between 5 to 10 lb of aluminum per MTU remains in the dissolver after coating removal and flushes. In the presence of nitric acid, aluminum is converted to Al(NO₃)₃ following the equation shown below:

where 0.15 moles of N_2O is produced for every mole of aluminum. Assuming 10 lb of aluminum are left in the solution per every MT, and a charge of 14.7 MTU, the total amount of aluminum left in the solution is 147 lb/run (66.7 kg/run). Therefore, the total amount of N_2O produced during the dissolution is 16.3 kg/run. The total N_2O in mg/m^3 and ppm units released to the air is given below for a 48-hour period.

$$Total_N_2O = \left(\frac{16.3 \times 10^6 \text{ mg}}{\text{run}} \right) \times \left(\frac{1 \text{ run}}{48 \text{ hr}} \right) \times \left(\frac{1 \text{ hr}}{60 \text{ min}} \right) \times \left(\frac{1 \text{ min}}{240,000 \text{ ft}^3} \right) \times \left(\frac{1 \text{ ft}^3}{0.0283 \text{ m}^3} \right)$$

$$= \frac{0.83 \text{ mg}}{\text{m}^3}$$

$$Total_N_2O = \frac{0.83 \frac{\text{mg}}{\text{m}^3} \times 24.45}{44} = 0.46 \text{ ppm}$$

In summary, the chemical reactions shown above demonstrate and estimate the average concentration in the production of NO , NO_2 , N_2O , and NH_3 during the decladding and dissolving process. Although it is known that the production and therefore the concentration of these effluents is time dependent, for calculation purposes it was assumed that the effluents were released in a constant manner in a time period of 48 hours.

Analyses of air samples with FTIR containing process effluents are hampered to great extent by the water content in the atmosphere. The infrared absorption spectrum of air is dominated by water absorption bands centered around 3700 and 1600 cm^{-1} and CO_2 absorption bands centered at 2348 and 667 cm^{-1} . Some of the compounds of interest in the PUREX process have absorption bands in the spectral locations of the H_2O and CO_2 absorption regions. The detection sensitivities using a 9.8-meter multipath cell for many of these compounds of interest are in the order of 0.01-1 ppm.

Figure 5 shows the spectra of NO , NO_2 , N_2O , HNO_2 . The vibrational band of NO located at 1876 cm^{-1} is the most difficult component to detect and quantify due to the water absorption band. Figure 6 shows a three-dimensional plot of the infrared absorption spectra acquired during the decladding and dissolution processes. The spectrum clearly shows the time dependence behavior for several chemicals. Careful examination of the time dependent spectra do not exhibit other time dependent effluents. Methane and CO_2 were found to be near ambient concentration levels. The NO , NO_2 , N_2O , HNO_2 , and SF_6 were quantified, and the results are shown in Table 3. Kr-85 data is in disintegrations per minute per 1 ml (dpm/cc) of air above background.

Table 3. Air samples concentration analysis (ppm). Kr-85 data is in dpm/cc of air

Sample	Day Collected	Time Collected	NO ₂	NO	N ₂ O x 100	HNO ₂ x 100	SF ₆ x 500	Kr (dpm/cc) (2 σ)		
WA1	11/4/96	0800	NM	NM	NM	NM	NM	NM	+/-	NM
WA2	11/4/96	0820	0	0	0	0	NM	NM	+/-	NM
WA3	11/4/96	1300	0	0	0	0	NM	5.4	+/-	3.0
WA4	11/4/96	2345	0	0	0	0	NM	8.6	+/-	3.0
WA5	11/5/96	0745	0	0	0	0	NM	6.1	+/-	3.0
WA6_A&B	11/6/96	1200	153	63	130	100	75	117.6	+/-	4.1
WA7_A&B	11/6/96	1400	84	27	128	120	153	111.8	+/-	4.1
WA8	11/6/96	1600	14.3	9	73	15	6	-0.6	+/-	2.9
WA9	11/6/96	2400	3.4	NM	23	NM	NM	-3.9	+/-	2.9
WA10	11/7/96	0800	4.2	NM	20	NM	NM	-5.0	+/-	2.8
WA11	11/7/96	1600	110	38	94	100	159	145.0	+/-	4.4
WA12	11/7/96	1800	83	6	120	110	NM	155.6	+/-	4.5
WA13	11/7/96	2000	14	NM	96	NM	NM	-7.2	+/-	2.8
WA14	11/7/96	2400	9	NM	69	NM	NM	27.6	+/-	3.2
WA15	11/8/96	0800	1.4	NM	29	NM	NM	-0.3	+/-	2.9

Figure 7 shows a plot concentration versus time for most effluents identified in Table 3. All the effluents showed a similar behavior for the first and second cuts. WA2, WA3, WA4, and WA5 air samples obtained during decladding process did not show the presence of any particular effluent. For all practical purposes, the air eluting the F-Canyon stack was natural air. Since NH₃ or ⁸⁵Kr was not present in the air samples, it was concluded that good isolation exists between the decladding process pipelines and the pipes leading to the main stack.

Ammonia was previously observed eluting from the dissolver stacks using passive FTIR by NTS. During the decladding phase on September 4, 1996, a Midac instrument in the passive configuration was deployed approximately 6 meters from the stack. The ammonia plume was measured against the skies. Figure 8 show the difference spectrum (plume-sky background) containing the ammonia "fingerprint". During the dissolution #9, the Aerospace and Army teams clearly identified ammonia from the dissolver stacks.

NO₂ was the effluent with the highest concentration detected in the air samples (153 ppm). Since the concentrations were not measured in real time, the NO₂ concentration is not necessarily representative of the stack's effluents since NO reacts in the air to produce NO₂. The highest concentration of NO was also found in the first cycle at 63 ppm. The highest concentration of NO_x (NO₂ + NO) was found in the first acid cut at 216 ppm. The NO₂ and NO graphs correlates in time. A close look at these two curves shows that when the NO₂ concentration drops in half or less, the NO has mostly disappeared. This effect was seen in the both cuts.

More information about the correlation of NO_2 and NO will be obtained during the real time studies using an NO_2/NO analyzer planned for dissolution #12.

The NO_x curves show a large concentration ratio between the peak of the first cut and the valley between the cuts. The concentration of NO_2 in WA9 is only 2 to 3% of the peaks of the first and second acid cuts (WA6 and WA11). NO shows a much wider gap between the cuts. The different width of the gap detected by monitoring NO_2 and NO suggests a concentration dependence efficiency of the scrubbers. The average release of NO_x to the air for a 14.7 MTU in a period of 48 hours was calculated at 180 ppm. The integrated concentration from the experiments show 32 ppm for NO_2 and 9 ppm for NO for total concentration of NO_x of 41 ppm. Therefore, approximately 23% of all NO_x is released through the stack to the atmosphere.

HNO_2 found in concentrations of 1 ppm correlates with the NO_2 profile. At present, it is not clear whether the HNO_2 is produced in the stack, the sampler plumbing, or the air bag. This dilemma can only be resolved using non-invasive technologies such as open-path FTIR.

The N_2O concentration profile is the most interesting of all. N_2O exists in the atmosphere at approximately between 0.3 to 0.4 ppm. The experiments showed N_2O ambient concentrations of 0.43 to 0.46 ppm in samples WA2, WA3, WA4, and WA5 (background and decladding process). During the dissolution process, N_2O is produced by aluminum left in the batch reacting with HNO_3 . It has been estimated that approximately 5 to 10 lb of aluminum per MTU is left behind in solution. An amount of 10 lb of aluminum per MTU should result in an integrated concentration of 0.46 ppm of N_2O for a 48-hour period. The studies indicate that approximately 0.61 ppm of N_2O was released to the air during the 48-hour dissolution process. The concentration of 0.61 ppm of N_2O can be correlated with approximately 199 lb of aluminum left in the dissolver after the decladding process. At a 10 lb of aluminum per MTU, we could estimate from the N_2O concentration measurement that 20 MTU were dissolved (only 14.7 MTU were dissolved in reality). All these estimates are based on the assumption that the only source for the production of N_2O is the reaction of aluminum with the HNO_3 during the dissolution process.

The concentration measurements also show that the valley to peak concentration of N_2O is approximately 19%. This ratio is different to the one obtained for NO_2 (3%) and much larger than the NO ratio. Since N_2O is relatively stable and cannot be converted easily to other nitrogen oxides (NO and NO_2 to HNO_3) in the canyon or the atmosphere, the concentration of N_2O may provide a better indicator for the amount of fuel dissolved at the canyon if the aluminum carryover from decladding is quantified.

The curves of N_2O versus NO_x and HNO_2 are very different. The curves demonstrate that different kinetics are followed in the production of N_2O and NO_x . Since the dissolver is a high-radiation source, a possibility for the photochemical formation of N_2O from NO_x in the dissolver was considered and eventually eliminated due to the different concentration profiles.

The ^{85}Kr activity profile provided a valuable piece of information in the understanding of the inorganic effluents released from the canyon. The ^{85}Kr profile clearly shows a similarity with the NO_x profile and therefore different to the N_2O profile. The ^{85}Kr concentration profile in the second acid cut is larger than in the first acid cut. The ^{85}Kr profile lags behind the NO_x concentration profiles. A burst of ^{85}Kr in air sample WA14 at the present is not understood. Similar ^{85}Kr results were obtained during the repeated analysis of WA13, WA14, and WA15 air bags eliminating the possibility of a measurement error. It is possible that the ^{85}Kr found in WA14 is the result of trapped bubbles in solution or in the pipes and released to the air during the solution transfers.

Finally, the presence of SF_6 was a surprise in these measurements. In a separate but simultaneous experiment, SF_6 was released to the annulus by the Aerospace group to image the plume eluting the stack. SF_6 mixes with the air from the stack at the top of the stack at approximately 200 ft above ground. The sampler is located at approximately 100 ft above the ground. In order to detect SF_6 in the samples, the most probable reason is a leak in the inner wall of the stack below the sampling port. Concentrations of SF_6 detected in the samples were in the order of 300 ppb, which may be used to estimate the leak rate.

Conclusions

Atmospheric effluent releases of NO_2 , NO , HNO_2 , N_2O , ^{85}Kr and SF_6 were identified and quantified during irradiated fuel and target reprocessing operations in the air samples collected at the F-Canyon stack. Concentrations of NO_x were well below concentrations predicted by mass balance (41 ppm vs. 180 ppm). The concentration of N_2O was closer the predicted value (0.61 ppm versus 0.46 ppm for a 10 lb per MTU left in the dissolver). The time dependence concentrations of NO_2 , NO , and N_2O , although follow the first and second cuts are different, suggesting perhaps a concentration dependence behavior of scrubbers. The N_2O concentration profile showed a different production kinetics than the NO_x concentration profiles. The N_2O concentration profile obtained in this experiment suggests that it is a better signature for the identification of the amount and type of fuel being dissolved in the canyon. N_2O_4 , N_2O_5 , HNO_3 , NH_3 , N_2H_4 inorganic compounds were not detected in this study. Other weak infrared absorption bands were found but not identified with any particular effluent. The detection of SF_6 added as a plume tracer indicated the presence of a leak in the stack inner wall.

It is important to realize that the integrated concentration values for the effluents are estimates since few points were obtained during the cycle profile. For example, the second acid cut according to operations started on 11/7/96 at 1300. The closest points we have are at 800 and 1600 hours. This discrepancy affects the curve and the area under the curve. More studies will be required to accurately determine the profile.

Figure 1. FTIR spectrometer/ multipath cell assembly

Figure 2. Absorption spectrum of WA7 sample

Figures 3a and 3b. Infrared absorption spectra of WA7 sample with water spectroscopically removed and with background subtraction (WA5)

Figure 3c. Amplification of small infrared absorption bands in Figure 3b

Figure 4. Simplified schematic of F-Canyon stack

Figure 5. Infrared absorption spectra of NO_2 , NO , N_2O and HNO_2

Figure 6. Three-dimensional plot (intensity-wavenumber-time)

Figure 7. Concentration plot versus time. Kr-85 data is in disintegrations per minute per ml of air (dpm/cc).

Figure 8. Passive spectrum of ammonia (plume-sky) and library reference