EVALUATION OF GAS-PHASE TECHNETIUM
DECONTAMINATION AND SAFETY RELATED EXPERIMENTS
DURING FY 1994. A REPORT OF WORK IN PROGRESS

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SUMMARY

This report documents the status of certain activities for fiscal year 1994 (October 1993 through September 1994); therefore, the results reported are incomplete and are of a preliminary nature. Laboratory activities for FY 1994 included several topics: (1) the evaluation of decontamination of technetium (Tc) by gas-phase techniques, which was initiated during FY 1994 and will continue next year, (2) the evaluation of diluted chlorine trifluoride (ClF_3) as a decontamination agent for removal of uranium deposits, (3) the evaluation of the potential hazard of wet air inleakage into a vessel containing ClF_3 , (4) the planning and preparation for experiments to help assess the hazard of a rapid reaction of ClF_3 and highly hydrated uranyl fluoride, (5) the planning and preparation for experiments to help assess the hazard of a rapid reaction of ClF_3 and powdered aluminum, and (6) the preliminary evaluation of the compatibility of Tenic valve seat material.

The lab facilities and safety document were modified to accommodate the Tc studies. Pertinent information on the chemistry and properties of Tc, including vapor pressure information on volatile Tc compounds, is reviewed within this report to support the experimental approach. Pertechnetyl fluoride (TcO_3F) and technetium hexafluoride (TcF_6) are two compounds with sufficient volatility that the Tc could possibly be decontaminated from contaminated surfaces if the Tc were converted to one of these compounds. TcF_6 is a much more desirable compound than TcO_3F from the standpoint of Tc gas-phase decontamination because of its much higher vapor pressure (224 torr at 77°F versus 31 torr for TcO_3F).

At present, the investigation of ^{99}Tc removal from metal samples by gas-phase treatment is in an early stage. The experiments to date have been short-term evaluations in the flow loop reactor for not more than 7 days and the only samples evaluated have been barrier tube and a brass fitting. Evaluations of gas-phase removal of Tc from contaminated barrier tube samples were done at 75°F, 120°F, 150°F, and 270°F in the flow loop with 4 psia of pure ClF_3 . The Tc may have first begun to move at 120°F, but the apparent movement was too slight to be conclusive. A reduction of beta/gamma (β/γ) emissions of between 21% and 29% was observed from the barrier tube samples after 5 days exposure to recirculating ClF_3 at 270°F. Although reductions of radioactive emissions have been noted from the samples with an increase of emissions on a blank test coupon and sodium fluoride (NaF) trapping material, a quantitative measure of the amount of Tc moved is not possible until radiochemical analysis of the samples can be completed.

One data point has been evaluated with the brass fitting sample using 4 psia of pure ClF_3 at 120°F. This treatment resulted in a considerable decrease in the alpha emissions, which were due to residual amounts of uranium; but the slight decrease in β/γ emissions was insufficient to conclusively indicate removal of ^{99}Tc from the sample. The evaluation of results to date are based upon radioactive emissions observed with a Ludlum 2000 instrument and based upon attempts to distinguish the low energy beta emissions of ^{99}Tc from the high energy emissions from ^{234}Th and ^{234}Pa . This is, at best, a rough method for identifying or quantifying ^{99}Tc , but it is presently the only rapid method available for our use. At this point in the evaluation, ^{99}Tc does not appear to be reacting readily with ClF_3 to form volatile Tc compounds. However, it is possible the Tc is volatilizing slowly. Radiochemical analysis are required before a quantitative measure can be made of the amount of ^{99}Tc on any of the samples.

Experiments to evaluate the effectiveness of diluted ClF_3 as a decontamination agent for removal of uranium deposits were conducted as a result of concerns that pure ClF_3 may be excessively reactive from a safety viewpoint under some hypothetical scenarios. The objective of these experiments was to determine if ClF_3 that is diluted with nitrogen and a fluorine additive will react readily enough with the uranium compounds of interest to be an effective decontamination reagent. The main conclusion from

six experiments using diluted ClF_3 was that the diluted ClF_3 will reduce the uranyl fluoride deposits to free-release levels; but because the amount of ClF_3 available for reaction is less when diluted ClF_3 is used, the ClF_3 is often consumed before all the uranium deposits are reacted if heavy deposits are encountered. An important disadvantage of using diluted ClF_3 from a safety viewpoint is that the diluent brings the initial total process gas pressure to nearly atmospheric pressure. This is undesirable because the process gas should be maintained at subatmospheric pressure to prevent outleakage of ClF_3 , but little margin remains for further increases in pressure due to reaction or inleakage of air if the initial process pressure is at nearly atmospheric pressure due to addition of the diluent.

A recent experiment using pure ClF_3 was also done for comparison to the runs using diluted ClF_3 . These results were also compared to the experiments done over a year ago also using pure ClF_3 . All experiments used uranyl fluoride samples from sections of the same copper seal exhaust line that was used in the previous series of experiments. The recent experiment using pure ClF_3 exceeded the reaction rate of the diluted ClF_3 as expected, but the recent experiments using pure ClF_3 and diluted ClF_3 showed a considerably more rapid rate of reaction than similar experiments done over a year ago using pure ClF_3 . The unusually high reaction rate noted during the recent experiments has been tentatively ascribed to a higher degree of hydration of the uranium deposit from which laboratory samples were taken. Increased hydration may have occurred due to absorption of moisture from air. An increased degree of hydration was indicated from the increased amounts of HF observed in the reaction product gases. The X-ray diffraction analyses of the uranyl fluoride also indicated that a change occurred over the last year that is compatible with increased hydration, but increased hydration was not conclusively proven from the X-ray diffraction results. The observed increased reaction rate suggests that the rate of gas-phase decontamination could possibly be increased by deliberately exposing the interior of the gaseous diffusion equipment to a controlled amount of water vapor. However, consideration of nuclear criticality concerns would likely preclude introduction of moisture into areas containing highly enriched uranium. The observed results warrant further investigation.

A lab evaluation of the potential hazard of wet air inleakage into a vessel containing ClF_3 was proposed. This evaluation would have addressed the concern that saturated air suddenly inleaking into a vessel containing a subatmospheric charge of ClF_3 may have catastrophic effects due to the highly exothermic reaction of ClF_3 and water. However, calculations contained in Appendix B conclusively demonstrated that due to the relatively small concentration of water in saturated air at room temperature, the integrity of the vessel would not be endangered under worst case conditions. Planning and preparations were made for two additional experiments that address safety issues concerning hypothetical reactions of ClF_3 with highly hydrated uranyl fluoride and with powdered aluminum, but these experiments have not been carried out due to the higher priority of other lab activities.

An evaluation of the compatibility of Tenic valve seat material with pure ClF_3 was conducted at temperatures up to 300°F. The evaluation is important because Tenic, a mixture of Teflon (PTFE) and nickel, has been proposed as the best material for valve seats that will be used in the gas-phase uranium recovery demonstration equipment. The Tenic seems to have withstood the treatment well, but post analysis of the samples has not been completed.

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1. INTRODUCTION

Technetium (^{99}Tc) was introduced into the operating cascades decades ago as part of a program to recycle fuel from nuclear reactors. Although the distribution of Tc within the cascades is not known precisely, significant amounts are expected to have concentrated in the K-27 building (especially the purge cascade), in perhaps portions of the K-29 building, and in the K-311-1 and K-310-3 sections of the K-25 building. Significant amounts of Tc are not expected in the K-31 and K-33 buildings because the barrier and other major equipment were removed and either replaced or decontaminated during the Cascade Improvement Program. Except for the K-311-1 and K-310-3 sections of K-25, the K-25 building is not expected to contain Tc because the other portions of the building were isolated from the enrichment cascade before the nuclear reactor returns were introduced at the K-25 Site.

Gas-phase decontamination of Tc from the interior of gaseous diffusion equipment (if feasible) offers advantages over other methods since it could be applied prior to disassembly of the equipment, thereby minimizing health physics and industrial hygiene personnel exposure concerns. A gas-phase decontamination method could also reduce costs and minimize waste generation. The ultimate goal of gas-phase decontamination is to remove the Tc to sufficient levels that the radioactive emissions are below the free-release levels specified in Regulatory Guide 1.86. The laboratory activities described in this report include the initial efforts to investigate gas-phase decontamination of Tc.

The project to conduct a full-scale demonstration of gas-phase removal of uranium deposits is presently at the equipment design stage. Also, safety analyses are being done. As a part of the safety analyses that were conducted earlier this year, certain safety concerns were identified for laboratory investigation. One hypothetical concern was that the proposed use of pure ClF_3 may be too reactive. ClF_3 diluted with nitrogen and fluorine was suggested as a possible alternative. Evaluation of diluted ClF_3 in the lab was consequently undertaken to determine if the reaction with uranium deposits would be excessively inhibited by the diluent. Also, the concern was raised that an excessively vigorous reaction of ClF_3 and water may occur if air saturated with water vapor suddenly leaked into the converter being decontaminated. (The process equipment and converter would be initially charged to subatmospheric pressure with ClF_3). Both of these concerns were investigated although the concern regarding inleakage of saturated air was resolved by calculations. Two other safety concerns were raised for which laboratory investigation may be required next year. In addition to the safety concerns, the compatibility of Tenic with ClF_3 was investigated to aid completion of the equipment design.

2. TECHNETIUM DECONTAMINATION EVALUATION

2.1 PERTINENT CHEMISTRY AND PROPERTIES

This section is not intended as an exhaustive review of relevant information on Tc, but the information contained here is sufficient to help explain the experimental approach taken, which is further described in a following section. A bibliography of articles pertinent to gas-phase removal of Tc is given in Appendix A. The Tc isotope contaminating the gaseous diffusion equipment is ^{99}Tc , which decays to stable ruthenium (^{99}Ru) by emission of a negative beta particle (electron). ^{99}Tc has a half-life of 2.12×10^5 yr and has a specific activity much greater than ^{235}U or ^{238}U as seen in the comparison of data in Table 1. The activities listed for the nuclides in Table 1 do not include the various radioactive daughters that are always present with uranium, but the activity of the Tc will always greatly exceed the activity of the ^{235}U or ^{238}U on a per unit mass basis even considering the contribution of their daughters. Notice that ^{234}U has a specific activity comparable to the ^{99}Tc . Since ^{234}U was concentrated with the ^{235}U in the high enrichment areas of the K-25 building, ^{234}U could present as great a radiological concern as ^{99}Tc in portions of the K-25 building. The specific activity of an isotope is significant to decontamination because the higher the activity of the isotope the greater must be the decontamination efficiency if the contaminated surface is to be cleaned to the radiological free release standard contained in Nuclear Regulatory Guide 1.86².

Table 1. Comparison of activity of ^{99}Tc to ^{234}U , ^{235}U , and ^{238}U

Isotope	Half-life ¹ (years)	Specific activity (dpm/ μg)	Decay ¹ mode	Decay particle ¹ energy (Mev)
^{235}U	7.04×10^8	4.76	α	4.68
^{238}U	4.47×10^9	0.74	α	4.27
^{234}U	2.46×10^5	13700	α	4.86
^{99}Tc	2.13×10^5	37800	$-\beta$	0.29

Technetium hexafluoride (TcF_6), technetium oxide tetrafluoride (TcOF_4), technetium trioxide fluoride (TcO_3F), and technetium dioxide trifluoride (TcO_2F_3) have sufficient volatility to be in cascade gas streams of an operating gaseous diffusion plant, but TcO_3F (often called pertechnetyl fluoride) is the only compound of Tc to be identified there³. The fact that Tc can be mobilized is obvious since otherwise it would not have transferred from the UF_6 feed cylinder or moved along the cascades. The movement along the cascade was, however, very slow. Several years were required for Tc to migrate from the feed point of the Paducah Gaseous Diffusion Plant to the UF_6 product. At the Portsmouth Gaseous Diffusion Plant, the time required was much longer ~ 20 yr⁴. The chemistry of the Tc within a gaseous diffusion plant cascade is apparently very complicated. Several theories have been advanced to explain the behavior of Tc within a cascade, but the reliability of the theories is uncertain. One theory, advanced by R. L. Farrar and reported by E. J. Barber³, suggests that a reversible complex may form between UF_6 and TcO_3F as follows:

Another theory, reported by E. J. Barber³, proposes the possibility of the formation of a maximum boiling azeotrope in the UF_6 - TcO_3F phase system. (The azeotropic solution has a much lower vapor pressure than the vapor pressure of UF_6 or TcO_3F separately).

Before Tc can be removed by a gas-phase technique, it must be in the form of a compound of sufficient volatility. Table 2 lists the vapor pressure of TcF_6 ⁵, TcO_3F ⁶, TcOF_4 ⁷, and UF_6 ⁸. As seen in the table, the vapor pressure of TcF_6 is about twice that of UF_6 at 77°F. If TcO_3F were present alone in an item requiring decontamination, its vapor pressure may be sufficient to allow its removal; but as mentioned above, interaction with UF_6 may greatly lower its effective vapor pressure. If the Tc could be converted to TcF_6 , gas-phase recovery of the Tc would be much enhanced.

Table 2. Vapor pressure data for TcF_6 , TcO_3F , TcOF_4 , and UF_6

Temp (C)	Temp (°F)	TcF_6 (Torr)	TcO_3F (Torr)	TcOF_4 (Torr)	UF_6 (Torr)
10	50	103.48	10.17	a	39.2
15	59	135.17	16.07	a	54.6
20	68	174.85	23.67	a	80.0
25	77	224.08	31.07	0.01	119.5
30	86	284.65	40.41	0.02	151.5
35	95	358.57	52.12	0.04	213.0
40	104	441.21	66.68	0.08	295.4
45	113	513.39	84.65	0.15	397.6
50	122	635.43	106.66	0.29	522.1
55	131	754.68	133.46	0.52	711.1
60	140	890.51	165.88	0.94	910.0

*Entry unavailable

TcF_6 can be prepared⁹ from Tc metal and fluorine gas at 400°C. Perhaps TcF_6 can be formed at lower temperatures with ClF_3 by reaction with the Tc compound(s) that exist in gaseous diffusion equipment. TcO_3F has been prepared by reaction of TcO_2 and fluorine at 150°C in a nickel tube. The volatile TcO_3F product was collected in a cold trap cooled by trichloroethylene-carbon dioxide slush.

Volatile Tc compounds can be collected by cold trapping and chemical trapping much like UF_6 can be collected; however, MgF_2 pellets are one of the few sorbent materials that offer the means to selectively remove the Tc from the UF_6 and other gases that may be present¹⁰. NaF will remove both gaseous Tc and UF_6 and allow the other gases, such as ClF_3 , to pass through the chemical trap. The chemical form of the Tc may have an important impact on the trapping effectiveness of the MgF_2 or NaF pellets. TcO_3F may be much more effectively trapped than TcF_6 ³. Activated alumina and several types of limestone make highly effective trapping material for gaseous Tc¹¹; but they do not allow selectivity in the gases they trap since they trap UF_6 and other fluorinating gases as well.

2.2 LAB FACILITIES AND SAMPLES

During initial planning for the evaluation of Tc decontamination in early FY-94, room B-102 of building K-1006 was assumed to be the lab in which the experiments would be conducted. This lab had been previously used for Tc experiments, and there was great reluctance to introduce Tc into K-1004L. Therefore, the lab hood stack permits, lab design, and other activities were initially pursued assuming a new lab would be built in K-1006. Due to a budget cut and changing health physics philosophy, permission was received to use the same lab in K-1004L for the Tc experiments that was used for conducting the uranium decontamination experiments. Overall this reversal of plans resulted in considerable net savings considering the expense of building new equipment for the lab in K-1006, but the time spent initially pursuing the establishment of the lab in K-1006 was lost.

The lab facilities are the same as those described in the feasibility report for gas decontamination of uranium compounds by E. B. Munday and D. W. Simmons¹² and will not be repeated in detail here. Briefly, an experimental flow loop is available which includes a reactor into which contaminated samples can be inserted for treatment. A small metal bellows pump circulates the process gases through the reactor and a Fourier Transform Infrared Spectrometer (FTIR) is used to monitor most gaseous constituents. The reactor can be heated as desired. Simpler reactors are also available that are called long term low temperature reactors (LTLT). They are used to expose samples to process gases for long periods without circulation of the gases.

An important precondition for using the K-1004L lab for Tc evaluation was that a completely separate gas feed manifold was required for the Tc test equipment to guarantee that Tc could not migrate from our equipment to other test equipment located in the same lab. (Previously our equipment shared a gas manifold with other equipment involved in a separate program run by another experimentalist). A surplus gas feed manifold was obtained that had been contaminated with UF₆ during experiments in another lab. This manifold was successfully decontaminated of the UF₆ by treatments with ClF₃ at room temperature, and the decontamination allowed it to be used as our feed gas manifold. This avoided the cost of constructing a new one, avoided disposal of a contaminated manifold, and added to our data on uranium decontamination at little additional cost.

The samples presently available for evaluation of Tc decontamination consist of several different materials and were obtained from the K-27 purge cascade area, which is known to be contaminated with Tc. These samples are also contaminated with uranium. The first samples obtained and evaluated were pieces of barrier tube. One of the problems encountered during Tc gas-phase decontamination experiments is measurement of the amount of Tc present. Due to the high activity of ⁹⁹Tc, an invisible quantity of the material may undergo high disintegration per minute (dpm) of beta radiation. The most convenient method for detection of ⁹⁹Tc is by survey with a beta radiation detector, but the beta radiation emitted by ⁹⁹Tc can be confused with the beta emitted by the ²³⁴Th and ²³⁴Pa daughters of ²³⁸U and other radionuclides. The beta emissions from ⁹⁹Tc are differentiated in a convenient but imprecise manner by first measuring the beta emissions with a survey meter and noting the reading, then repeating the measurement with a thin rubber shield over the meter probe and comparing the two readings. Since the beta emissions from ⁹⁹Tc is of low energy compared to other beta emissions, the rubber shield will significantly block the emissions if ⁹⁹Tc is the emission source. The only method available to us at present for quantitative determination of ⁹⁹Tc involves dissolving a sample, separating the ⁹⁹Tc from other radionuclides by extraction chromatography, and then determining the amount of ⁹⁹Tc by liquid scintillation techniques¹³. Unfortunately, this is a slow method. We hope to have improved methods for quantifying the ⁹⁹Tc contamination soon.

Table 3 lists measured radioactive emissions of the samples presently available. None of these samples have visible Tc deposits. All have low alpha readings (the free-release level is 5,000 dpm/100 cm²) which indicates little uranium is present. The relatively high beta readings in comparison to the low alpha readings also is an indication that ⁹⁹Tc is present.

Table 3. Radioactive emissions from untreated samples

Sample		Alpha ^a (dpm/100cm ²)	Beta/Gamma ^a (dpm/100cm ²)
1.	Barrier	150	49,800
2.	Barrier	150	44,200
3.	Flange gasket	1100	140,700
4.	Flange gasket	260	28,800
5.	Flange gasket	70	14,000
6.	Flange gasket	100	25,200
7.	Copper tubing (outside reading)	<60	9,000
8.	Brass fitting	160	315,100
9.	Valve cover	<60	2,800

^aAll measurements taken with a Ludlum instrument as point sources.

2.3 EXPERIMENTAL APPROACH AND RESULTS TO DATE

Since gaseous diffusion experience clearly indicates that Tc is mobile to a significant extent, the gas-phase experiments seek to identify conditions under which the natural mobility of Tc can be improved. Considering the vapor pressure data on different Tc compounds contained in Table 2, the chemical form of the Tc has a very important impact on the feasibility of gas-phase Tc removal. Unfortunately, the very small amounts of Tc involved make identification of the Tc compounds present on the metal surfaces or present in the process gas extremely difficult. During the gas-phase uranium decontamination experiments, gram quantities of uranium compounds were present, which are sufficient amounts for x-ray diffraction analysis. Also, the UF₆ generated by reaction with ClF₃ could be easily detected on the FTIR and the quantity of UF₆ estimated. Unfortunately, neither x-ray diffraction nor the current FTIR gas cell can be used to monitor the Tc due to the minute amounts present. (A long path cell used in the FTIR would be capable of improving Tc detection to the level of 5 to 10ppm of TcO₃F or TcF₆). The lab experiments must be done under the limitations that the chemical form of the original deposit and the Tc volatilized to the gas-phase cannot be identified. The beta emissions of the ⁹⁹Tc are relied upon to a considerable extent as an indication of the presence and quantity of the ⁹⁹Tc present. This is at best a very approximate method for reasons mentioned in the previous section; also, the low energy beta emitted by ⁹⁹Tc can be fairly easily shielded so the measured beta radiation is not a good indicator of the total present. Although the lab equipment does not allow for real-time analysis of the Tc, the presence and quantity of ⁹⁹Tc can be accurately measured by radiochemical methods but only after the sample subsurface is dissolved in an acid solution.

Although the Tc present in the operating cascades is believed to be in some form of TcO_3F (perhaps the TcO_3F is complexed with UF_6), the Tc on the metal samples that have been exposed to the atmosphere for long periods cannot be in the form of TcO_3F , because a compound with the vapor pressure of TcO_3F would have already dissipated from the metal surface. Apparently, exposure of TcO_3F to air converts it to a less volatile compound. One of the first points of interest is whether concentrated ClF_3 at room temperature or higher would readily react with the Tc and convert it to a volatile Tc compound (hopefully TcF_6).

The barrier tube samples were the first samples evaluated. Two pieces of barrier tube sample were surveyed with Ludlum instruments for both alpha and beta/gamma readings before placing them in the test loop reactor. All evaluations to the present time have used pure ClF_3 at 4.0 psia at various temperatures. The first temperature evaluated was 75°F. After placing the samples in the reactor, air was evacuated from the system and the ClF_3 was administered. The metal bellows pump circulated the ClF_3 slowly around the flow loop through the reactor and the FTIR. During the Tc evaluations, the FTIR was used to monitor the ClF_3 , but as previously mentioned, the amounts of Tc on the samples were too small to expect an indication on the FTIR even assuming all the Tc volatilized. The first test was run for 2 days, then the ClF_3 was evacuated and the samples were removed for resurveying, which indicated no significant change in the reading. A summary of all the tests with the barrier tube is shown in Table 4. The same samples were then returned to the reactor and the evaluation repeated at 75°F for 7 days upon which time they were removed and surveyed again. Following the exposure to ClF_3 for the additional 7 days, the alpha emissions decreased >32%, indicating that some of the small amount of uranium in the barrier was removed; however, the beta/gamma readings changed very little, indicating insignificant removal of the Tc.

Following the evaluations at 75°F, the same two samples were returned to the flow loop reactor and exposed to ClF_3 at 120°F for 7 days. The samples were removed from the reactor for resurveying after each evaluation described below and replaced in the reactor for evaluation at the next temperature. This exposure resulted in a >15% reduction of the beta/gamma readings, which indicates that some Tc may have been removed. During this 7-day period, a small amount of UF_6 was added to the reactor for calibration of the FTIR. Some of the UF_6 was absorbed by the barrier tube samples, and the absorption of UF_6 resulted in an increase of alpha emissions. The absorption of UF_6 is apparent in Table 4 by comparison of the alpha emissions following the evaluation at 75°F (103 dpm/100 cm² for sample 1 and 97dpm/100cm² for sample 2) with the emissions following the evaluation at 120°F (349 dpm/100 cm² for sample 1 and 223 dpm/100 cm² for sample 2). The same barrier tube samples were exposed to ClF_3 at 150°F for 5 days which removed most of the small amount of uranium that was deposited during the UF_6 calibration procedure at 120°F. The beta/gamma emissions showed only a slight change as a result of the 150°F treatment. The samples were then exposed to ClF_3 for 5 days at 270°F which further reduced the already very low alpha readings to lower levels and significantly reduced the beta/gamma levels. Sample 1 decreased from 41,500 dpm/100 cm² to 29,200 dpm/100 cm² (a 29.6% reduction) and sample 2 decreased in beta/gamma emissions from 34,500 dpm/100 cm² to 27,000 dpm/100 cm² (a 21.7% reduction). Over the entire series of experiments from 75°F to 270°F, the two barrier tube samples were exposed to 4 psia of ClF_3 for a total of 26 days and the beta/gamma emissions decreased from 48,800 dpm/100 cm² to 29,200 dpm/100 cm² for sample 1 (a 41.4% reduction) and from 44,200 dpm/100 cm² to 27,000 dpm/100 cm² for sample 2 (38.9% reduction).

A quantitative determination of the amount of ⁹⁹Tc removed must await radiochemical analyses of the samples. A blank copper test coupon and a small container of NaF pellets were also placed in the test loop reactor downstream of the barrier tube samples. Radioactive material clearly transferred to the NaF

Table 4. Tabulation of radioactive emissions from barrier tube samples before and after each test condition

Treatment condition ^a	Sample No.	Alpha (dpm/100 cm ²)	Unshielded beta/gamma (dpm/100 cm ²)	Shielded ^b beta/gamma (dpm/100 cm ²)	% change in unshielded beta/gamma reading from previous treatment
Initial	1	152	49,800	10,400	
	2	152	44,200	14,500	
After 2 days @ 75°F	1	152	50,500	d	+1.4
	2	145	40,300	d	-8.8
After 7 additional days @ 75°F	1	103	47,546	d	-5.8
	2	97	41,663	d	+3.4
After 7 days @ 120°F	1	349 ^c	39,500	d	-16.9
	2	223 ^c	35,400	d	-15.0
After 5 days @ 150°F	1	90	41,500	8,700	+5.1
	2	76	34,500	8,000	-2.5
After 5 days @ 270°F	1	46	29,200	9,000	-29.6
	2	35	27,000	8,000	-21.7

^aAll treatments used 4.0 psia of pure ClF₃.

^bThe beta/gamma probe was shielded with a 7-mil-thick piece of latex as an indication of low energy beta of ⁹⁹Tc origin.

^cThe increase in alpha readings at this point was due to the addition of a small amount of UF₆ for calibration of the FTIR.

^dReading not taken.

pellets and copper disk as a result of the experiment, but it will not be possible to determine all ⁹⁹Tc removed from the barrier tube by analysis of these materials because ⁹⁹Tc undoubtedly also transferred to other surfaces within the reactor and probably around the flow loop. The Ludlum instrument readings of the copper disk indicated very low alpha emissions of 14 dpm/100 cm² (probably due to uranium) and much higher beta/gamma emissions of 7,700 dpm/100 cm² (presumably due to transfer of ⁹⁹Tc but some of the beta radiation could be due to ²³⁴Th and ²³⁴Pa). The surface readings of the NaF pellets also indicated a transfer of radioactive material from the samples to the NaF pellets. The alpha readings were 78 dpm/100 cm² and the beta/gamma readings were 3,000 dpm/100 cm². Perhaps the beta/gamma emissions noted from the NaF pellets are lower than that noted on the copper coupon because the ⁹⁹Tc was absorbed below the surface of the porous NaF pellets resulting in partial shielding of the emissions.

The brass fitting, sample 8 shown in Table 3, is also being evaluated for gas-phase decontamination. At the time of this writing it was subjected to 4.0 psia of pure ClF₃ at 120°F in the flow loop for 76 hr. The results are shown in Table 5. Two sets of alpha and beta/gamma readings were measured from the ends of the brass fitting. Location 1 shows considerably higher alpha emissions than location 2, which indicates the presence of more uranium at location 1. Location 1 also shows considerably less beta/gamma emissions than location 2. The high beta/gamma emissions (387,686 dpm/100 cm²)

measured at location 2 are presumed to be due to ^{99}Tc although planned radiochemical analysis has not been completed. The treatment apparently removed the large majority of the uranium at location 1 as indicated by the decrease in alpha emissions from 3,140 dpm/100 cm² to 284 dpm/100 cm²; but there is little ^{99}Tc movement since the beta/gamma readings only decreased slightly at location 2 (i.e., 387,686 dpm/100 cm² to 345,419 dpm/100 cm²).

**Table 5. Radioactive emissions from brass fitting
before and after evaluation**

Treatment condition	Location	Alpha (dpm/100 cm²)	Beta/gamma (dpm/100 cm²)	% change in beta gamma
Initial	1	3,140	55,242	a
	2	476	387,686	a
After 72 hrs. @120°F	1	284	52,726	-4.6
	2	145	345,419	-10.9

^aReading not applicable.

3. STUDIES RELATED TO SAFETY ISSUES OF CONCERN TO GAS-PHASE URANIUM DEPOSIT REMOVAL

3.1 EVALUATION OF DILUTED CHLORINE TRIFLUORIDE

This series of experiments was conducted to evaluate the decontamination efficiency of diluted ClF_3 , and to compare the efficiency of the diluted ClF_3 to that of pure ClF_3 . Two different conditions were evaluated: 1) 20.7% by volume ClF_3 , 8.9% F_2 , and 70.5% N_2 at a total pressure of 700 torr (13.54 psia) and 2) 29.5% ClF_3 , 8.9% F_2 , and 61.6% N_2 at a total pressure of 700 torr. One sample was run at each of the two different conditions in the flow loop reactor to allow observation of the rate of depletion of the ClF_3 and the rate of generation of the UF_6 as the reaction occurs. Additionally, two samples were run at each of the two different conditions in separate LTLT reactors. Also, one sample was run in the flow loop reactor with pure ClF_3 at 4.0 psia. All 7 experiments were conducted near 75°F. The results of these experiments is summarized in Table 6. All samples used in these experiments were obtained from sections of the same seal exhaust line that supplied samples for the feasibility study.¹² The experiments were conducted in the same manner as in the feasibility experiments, and details for carrying out the experiments are described in the feasibility report.¹²

Table 6. Summary of uranium removal experiments using diluted ClF_3 ,

Sample No. ^a	Initial % gas composition			Total pressure (torr)	Number of separate charges ^b	Total reaction time (days)	Amount and % of U^c removed	
	ClF_3	F_2	N_2				(g)	(%)
TLDL01	20.7	8.8	70.5	700	4	15.40	3.382	>99.9
TLDL02	100.0	0.0	0.0	207	2	10.00	3.200	>99.9
TLDL03	29.5	8.9	61.6	700	1	1.04	2.782	>99.9
LTDL01	29.5	8.9	61.6	700	2	60.00	e	e
LTDL02	20.7	8.8	70.5	700	2	60.00	0.707	>99.9
LTDL03	20.7	8.8	70.5	700	4	d	e	e
LTDL04	29.5	8.9	61.6	700	3	d	e	e

^aTL denotes that the sample was evaluated in the flow loop reactor. LT denotes that the sample was evaluated in a LTLT reactor containing noncirculating gas.

^bThe reactor was evacuated and recharged the indicated number of times.

^cThe uranium is chiefly in the form of UO_2F_2 .

^dIncomplete.

^eReading not taken.

As seen in Table 6, all of the tests run with diluted ClF_3 were successful in removing the uranium to very low levels, which is nominally shown in the table as >99.9% removal. The results of the last two samples (LTDL03 and LTDL04) are not yet complete, but preliminary data indicates that similar results will be seen for them. Table 7 contains a summary of the radiation measurements taken with a Ludlum 2000 scaler instrument of the alpha and beta/gamma emissions before treatment, immediately following the completion of the treatment, and after an extended time following the completion of the treatment, called

Table 7. Summary of radioactive emissions from samples

Sample No.	Rad. readings before decontamination (dpm/100cm ²)		Rad. readings immediately after decontamination ^b (dpm/100cm ²)		Rad. readings after decay period ^b (dpm/100cm ²)		
	α	β/γ	α	β/γ	Time (days)	α	β/γ
TLDL01	1,050	177,000	25	17,800	120	55	770
TLDL02	1,040	177,000	186	107,000	110	23	610
TLDL03	1,170	171,000	143	3,750	87	80	680
LTDL01	780	156,000	c	c	90	<10	460
LTDL02	880	111,000	c	c	90	<10	400
LTDL03	970	122,000	c	c	d	d	d
LTDL04	1,080	118,000	c	c	d	d	d

^aThe before-treatment readings are approximations because the tube sections were not split open until after treatment. Also, the alpha readings will be much lower than the true activity because a uranium deposit is self-shielding to alpha radiation.

^bBoth the Ludlum alpha meter and the Ludlum beta-gamma meters read *counts per minute*. The *counts per minute* readings must be multiplied by both an efficiency factor and a geometry factor to convert the readings to dpm/100 cm². The efficiency factor varies slightly with different instruments but is ~8.3 for the alpha meter and ~5 for a beta-gamma meter. If the object being surveyed is significantly smaller in area than the meter probe, the geometry factor is 1 for either meter type, and the object is called a *point source*. If the object is not significantly smaller in area than the probe, the geometry factor is 2 for the alpha meter and 6 for the beta-gamma meter, and the object is called a *plane source*. The lab samples are considered point sources, but the readings expressed as dpm/100 cm² are well below the free-release criteria of 5,000 dpm/100 cm² even if the plane source multiplier were used.

^cReading not taken.

^dData not available at time of writing.

the decay period. The beta/gamma radiation always continues to decrease following removal of the uranium because the ²³⁴Th and ²³⁴Pa daughters of ²³⁸U decay rapidly without replenishment after removal of the ²³⁸U. Pertinent radioactive decay information is available in Appendix C of the feasibility report.¹² Since the samples are cut from a section of a copper seal exhaust line (a 5/8-inch copper tube), the radiation readings taken before decontamination were observed by holding the probe of the Ludlum instrument to an end of a copper tube section that was cut from the main tube section as a sample. For this reason, the readings before decontamination are considerably lower than the true emissions rate. Also, the uranium deposit itself is self-shielding, which also tends to make the reading lower than the actual disintegrations per minute. Following decontamination, the sample tube section was cut apart lengthwise and flattened to obtain a more accurate reading. The radiation readings following a decay period are very low as seen in Table 7. All the readings shown in the table were obtained by using point source geometry factors on the Ludlum instrument since the samples are small, but the emissions would still be considerably below the free-release level of 5,000 dpm/100 cm² if the greater plane source geometry factor was used. (See footnote b at the bottom of Table 7 for an explanation of point source versus plane source multipliers.)

Table 6 indicates considerable difference in the reaction time for decontamination of the samples, with one sample, TLDL03, reacting to completion in 1.04 days (25 hr) and LTDL01 and LTDL02 reacting to completion in <60.0 days. The shorter observed reaction time for TLDL01, TLDL02, and TLDL03

as compared to the other samples is more a function of the ability to monitor reaction progress with the FTIR in the flow loop reactor than any other consideration. (Sample numbers starting with TL were reacted in the flow loop and sample numbers starting with LT were reacted in a LTLT reactor without FTIR online monitoring capabilities.) The ability to monitor the process gases with the FTIR decreases the reported reaction time because depletion of ClF_3 can be determined as it occurs, which allows for timely addition of more ClF_3 and because the depletion of the uranium deposit can be determined as it occurs. The observed reaction time in the LTLT reactors was longer than the true reaction time because the reaction ended sometime before gas samples were removed for analysis.

Figure 1 is a plot based on data taken with the FTIR (percent uranium remaining versus time) for the reaction of samples TLDL02 and TLDL03. Also, data points for a sample (TL3005C) reacted with 4 psia of ClF_3 at 75 °F during the feasibility experiments¹² is included for comparison to the recent experimental data. Several interesting observations can be made from Figure 1, which also illustrates the usefulness of an FTIR for monitoring reaction progress. Table 5 indicates that sample TLDL03 was decontaminated in only 1.04 days whereas sample TLDL02 was decontaminated in 10.00 days. This is difficult to understand without the aid of the FTIR data, since sample TLDL02 was subjected to 100% ClF_3 whereas sample TLDL03 was subjected to 29.5% ClF_3 . From Figure 1 it is apparent that initially the pure ClF_3 (hollow square) was reacting faster than the diluted ClF_3 (solid square); but the ClF_3 was consumed during the experiment initially charged with pure ClF_3 , whereas the ClF_3 was not all consumed during the experiment initially charged with diluted ClF_3 . A second charge of pure ClF_3 was later applied to sample TLDL02 to complete the reaction.

Another interesting observation from the plots contained in Figure 1 is that the reaction rates of samples TLDL02 (100% ClF_3) and TLDL03 (29.5% ClF_3) both greatly exceeded the reaction rate of TL3005C (100% ClF_3 data from over a year ago). Samples of the UO_2F_2 were submitted for analysis to allow comparison to the original analysis that were done over a year ago to try to identify the cause of the different reaction rates. X-ray diffraction of the uranium deposits has confirmed that a change has occurred in the sample (presumably greater hydration), but absolute identification of the material has not been confirmed. Additional hydration could have occurred because of the copper tube containing the uranium deposit has been exposed to the atmosphere since its removal from the K-33 cascade prior to conducting the feasibility study. Figure 2 is a plot of the same data shown in Figure 1 except Figure 2 is plotted on a log scale. The plot of the percent uranium remaining versus reaction time is seen to be approximately a straight line at least initially, which indicates a first order rate of reaction.

Table 8 contains initial reaction rate information for the experiments using diluted ClF_3 and pure ClF_3 . Also, initial reaction rate information is included from the feasibility experiments a year ago using pure ClF_3 . This reaction rate information clearly shows a much faster rate of reaction for the recent experiments as compared to the experiments run over a year ago. Also, there is a clear difference in the mole ratios of HF to UF_6 and ClF to UF_6 generated that strongly suggests a higher degree of hydration of the samples that were recently run compared to the samples run during the feasibility experiments. This further suggests that the UO_2F_2 in the seal exhaust line may have absorbed additional water since the last experiments resulting in higher reaction rates.

Figure 3 is a series of plots of the various process gas components seen during the reaction of $\text{UO}_2\text{F}_2 \cdot \text{H}_2\text{O}$ with ClF_3 . The UF_6 , ClF , ClO_2F , and HF are all by-product gases. The particular reaction shown in Figure 3 is the decontamination of sample TLDL03 which did not totally deplete the ClF_3 .

Diluted ClF_3 Treatment of Uranyl Fluoride

Fig.1 Plot of percent uranium remaining versus time for three data points.

Diluted ClF_3 Treatment of Uranyl Fluoride

Fig.2 Plot of percent uranium remaining versus time for three data points on log scale.

Table 8. Comparison of rate data for reaction of ClF_3 and UO_2F_2 taken under different conditions and at different times.

Sample	Treatment Condition		Initial ClF ₃ : UO ₂ F ₂ mole ratio	Consumed ClF ₃ :UO ₂ F ₂ mole ratio	Initial reaction rate K @ 4 hr (hr ⁻¹)	t _{1/2} @ 4 hr	HF:UF ₆ mole ratio	ClF:UF ₆ (ClO ₂ F) mole ratio
FY94								
TLDL01	2.8 psia ClF ₃ 1.2 psia F ₂ 9.5 psia N ₂	@ 75F	2.18	3.56	0.197 ± 0.006	3.52	1.38	2.05 (1.52)
TLDL02	4.0 psia ClF ₃	@ 75F	3.30	3.53	0.275 ± 0.007	2.52	1.21	2.20 (1.39)
TLDL03	4.0 psia ClF ₃ 1.2 psia F ₂ 8.3 psia N ₂	@ 85F	3.72	3.63	0.171 ± 0.004	4.05	1.30	2.57 (1.39)
FY92								
TL3005 ^a #3-3	4.0 psia ClF ₃	@ 80F	3.79	2.25	0.028	24.75	0.21	1.23 (0.85)
TL3001 ^a #3-1	4.0 psia ClF ₃	@ 80F	4.72	2.69	0.034	20.38	0.17	1.30 (0.96)
TL3004 ^a #3-2	4.0 psia ClF ₃	@ 150F	4.13	2.24	0.102	6.79	0.14	1.19 (0.81)

^aThese experiments were conducted in FY92 and are included here for comparison to the recent data.

Fig.3. Plots of gas constituents during a reaction in which all ClF_3 is not depleted.

CHANGE IN GAS CONCENTRATION
DURING GAS PHASE TREATMENT

Fig.4. Plots of gas constituents during a reaction in which all ClF_3 is depleted.

As seen on the plots, the ClF_3 concentration decreases rapidly initially and the concentrations of the by-product gases increase as the ClF_3 decreases. Towards the end of the reaction all plots develop a more horizontal slope. Figure 4 is a similar series of plots of the various gas compositions for decontamination of sample TLDL01. The plots in this figure illustrates an example of a decontamination process in which all ClF_3 is consumed before all of the uranium deposit is reacted. After 8 hours of reaction, the ClF_3 is nearly depleted and the ClF , which is also a strong fluorinating agent, can be seen to react with the uranium deposit as well as ClF_3 . The UF_6 , ClO_2F , and HF concentrations continue to slowly raise as the ClF concentration decreases.

3.2 EVALUATION OF THE HAZARD OF WET AIR INLEAKAGE

During preliminary safety reviews and the Hazardous Operations Study for the gas-phase deposit removal project, a hazard was hypothesized that air saturated with water vapor may suddenly inleak into a vessel containing ClF_3 at subatmospheric pressure resulting in sufficient heat generation to pose an unusual hazard. To help address this hazard, an experiment was proposed to measure the heat generation upon inleakage of saturated air into a lab reactor containing ClF_3 . As part of the preparations for this experiment, calculations (contained in Appendix B) were done to approximate the theoretical increases in gas temperature and pressure that could be expected due to the reaction of ClF_3 with the water contained in saturated air at 75°F. The amount and concentration of water in saturated air at 75°F was calculated (0.0158g water per liter of air). The heat of reaction of ClF_3 and water was used to calculate the temperature and pressure increase of the air that could occur assuming saturated air instantly fills a vessel initially containing 4 psia of pure ClF_3 and all of the water reacts instantaneously with ClF_3 with no heat transfer to the metal vessel walls. The calculations show that under the worse-case assumptions, the temperature of the air would not increase more than 337.5°C, and the pressure would not increase more than 22.8 psia. This temperature and pressure rise would not be expected to endanger the integrity of the vessel walls, which are 1/4-inch steel. Under real circumstances, the saturated air could not instantly fill the vessel and considerable heat transfer would occur from the gas to the metal vessel walls during the reaction; therefore, the actual temperature and pressure rise expected would be considerably less than the calculated values. The worst effect of inleakage of saturated air into the vessel would be that the vessel internal pressure could increase above atmospheric pressure and gases could then leak out of the vessel. As a result of these calculations, the lab experiments are considered unnecessary.

3.3 PLANNING AND PREPARATION FOR ADDITIONAL SAFETY RELATED EXPERIMENTS

Planning and preparations were made for two additional experiments that address safety concerns of hypothetical reactions of ClF_3 with either highly hydrated uranyl fluoride or with powdered aluminum. The concern is that an excessively vigorous reaction could occur with either of these materials and ClF_3 during gas-phase removal of uranium deposits.

The uranyl fluoride (UO_2F_2) that has been reacted with ClF_3 as part of the previous lab experiments was hydrated to perhaps as much as 1.6 molecules of water per molecule of UO_2F_2 . This state of hydration did not react rapidly enough with ClF_3 to generate much heat. The possibility exists that UO_2F_2 of greater hydration may be present in a converter due to inleakage of moisture over the decades since the K-25 cascade has been closed down. For this reason, an experiment was proposed to evaluate the heat generation from reaction of ClF_3 with specially prepared UO_2F_2 of highly hydrated form.

Similar concerns were expressed about the possibility of highly exothermic reactions between ClF_3 and

powdered metal that may be present in gaseous diffusion equipment due to rubbing of metal surfaces in gas compressors or due to slow corrosion of metal surfaces. In addition to the direct reaction of ClF_3 and powdered metal, the possibility was suggested that moisture could act as an initiating agent for rapid reaction with the powdered metal. Experiments were therefore proposed to evaluate the heat generation upon reaction of ClF_3 and powdered aluminum that was previously cooled and then subjected to saturated air to allow condensation of moisture on the aluminum.

A more detailed description of the experiments to evaluate the heat generation upon reaction of highly hydrated uranyl fluoride with ClF_3 is given in Appendix C. A more detailed description of the experiment to evaluate the heat generation upon reaction of powdered aluminum with ClF_3 is given in Appendix D. Appropriate thermodynamic calculations that were done as part of the Project Safety Summary documentation to authorize these experiments in the K-1004L lab are also included in the appendices. These laboratory experiments will not provide complete answers to the safety questions because of the large differences in scale and process conditions between the lab-scale experiments and the full-scale deposit removal activities. Also, our lab is not equipped with calorimetry equipment that would allow all heat generated to be measured.

These proposed experiments are rough approximations to hypothetical conditions that may or may not exist in the gaseous diffusion equipment. Successful completion of these experiments without occurrence of unusually vigorous reactions will not conclusively prove that vigorous reactions could not occur under full-scale process conditions. Possibly the safety concerns addressed by these experiments can be better resolved by more detailed thermodynamic calculations. This possibility will be further explored prior to proceeding with the experiments.

Although these experiments were not run this fiscal year, the equipment necessary to conduct the experiments was obtained or fabricated. Some of the equipment has not been installed to avoid the unnecessary potential contamination with Tc.

4. COMPATIBILITY OF TENIC VALVE SEAT MATERIAL WITH CHLORINE TRIFLUORIDE

The evaluation of Tenic valve seat material is important because this material has been proposed for use in the equipment presently being designed for the gas-phase deposit removal demonstration. A sample of the material was first evaluated briefly in the flow loop reactor with 4 psia of pure ClF_3 at 75°F, 120°F, 150°F, 200°F, and 300°F while monitoring the gas with the FTIR for signs of reaction. There was no sign of reaction during the 3 day period in which the temperature was incrementally increased from 75°F to 300°F. The sample was then removed from the flow loop reactor and put in a LTLT reactor and subjected to 4.0 psia of pure ClF_3 at 200°F for 55 days. A second sample of Tenic was placed in a second LTLT reactor and subjected to 4.0 psia of pure ClF_3 at 250°F for 45 days. There is no apparent deterioration of the material as a result of these tests, but stress tests to evaluate embrittlement have not been completed.

5. CONCLUSIONS AND RECOMMENDATIONS

At present, the investigation of ^{99}Tc removal from metal surfaces by gas-phase treatments is in an early stage. The experiments to date have been short-term evaluations in the flow loop reactor for not more than 7 day periods. Two barrier tube samples and a brass fitting have been used as samples. Quantitative analysis of the samples is not available at present. The evaluations of gas-phase removal of Tc from contaminated barrier tube samples were done at 75°F, 120°, 150°, and 270° in a flow loop reactor with 4 psia of pure ClF_3 . A reduction (~16%) in beta/gamma readings was first noted at 120°F but a similar reduction was not observed at 150°F. Since the uranium daughters also emit beta/gamma radiation, the noted 16% decrease in radiation is too small to be conclusively attributed to removal of ^{99}Tc . A reduction of beta/gamma emissions of between 21% and 29% was observed from the barrier tube samples after a 5 day exposure at 270°F. The beta/gamma readings taken with a Ludlum scalar instrument are at best a crude measure for ^{99}Tc since the uranium daughters also emit beta radiation. Radiochemical analysis are needed to quantify the amount of ^{99}Tc present.

An evaluation of gas-phase removal of ^{99}Tc from a brass fitting is in progress at the time of this writing. The one data point taken so far used pure ClF_3 at 4 psia and 120°F and resulted in considerable reduction in alpha readings which indicates that the already small amount of uranium present was reduced even more; however, there was little indication that the ^{99}Tc moved to a significant extent. Although the results to date are difficult to interpret due to lack of quantitative analysis of ^{99}Tc , the ^{99}Tc apparently is not showing a strong tendency to assume the gas-phase in the presence of pure ClF_3 . Due to the high activity of ^{99}Tc , highly contaminated samples often contain only trace amounts of ^{99}Tc which makes online detection and quantification of volatile ^{99}Tc compounds such as TcO_3F and TcF_6 difficult if not impossible. Since the experiments to this point have been fairly short term (<7 days) and since we presently cannot detect the ^{99}Tc in the gas-phase even if it is volatilized, it is possible that the ^{99}Tc may be slowly volatilizing. Longer term experiments should be ran to help evaluate this possibility. A copper jumper line has been located in the purge cascade area of K-27 which is known to have had high concentrations of ^{99}Tc flow through it. This line should be sectioned for samples for a future series of experiments since the sections from this line will provide more or less homogenous samples to allow comparison of results. The practicality of conducting experiments using measurable quantities of ^{99}Tc in our lab should also be investigated. The possibility that UF_6 may suppress the formation of volatile ^{99}Tc compounds, and the theory that hot air or nitrogen may be as effective as ClF_3 in moving ^{99}Tc should be investigated.

The evaluation of diluted chlorine trifluoride as an alternate for pure ClF_3 indicates that ClF_3 diluted to 20.7% or 29.5% with ~8.8% F_2 and the remainder N_2 gas successfully decontaminated the UO_2F_2 samples, though at a somewhat slower rate than pure ClF_3 . Recent experiments with diluted and pure ClF_3 proceeded considerably faster than the experiments run under the same conditions with pure ClF_3 over a year ago. Samples are being analyzed in an attempt to understand the results. This investigation should continue.

Calculations performed to support experiments to evaluate the potential hazards of wet air leakage into a vessel containing a subatmospheric charge of ClF_3 showed conclusively that due to the relatively small amount of water in saturated air, insufficient heat or pressure would be generated to endanger the vessel. The worse expected consequences would be pressurization of the vessel followed by outleakage of ClF_3 . The experiments to measure the heat generated upon inleakage of saturated air into a vessel containing ClF_3 were canceled as unnecessary.

Planning and preparations were made for two experiments that address safety concerns of hypothetical reactions of ClF_3 with either highly hydrated uranyl fluoride or with powdered aluminum. These experiments were proposed due to safety concerns arising from Engineering Safety Analyses earlier this year. Since that time, additional calculations have been done for the Engineering Safety Department that may have an impact on changes to these experiments. These experiments are candidates for evaluation next year, but the experiments should be reevaluated.

The evaluation of the Tenic valve seat material has indicated no obvious detrimental effects upon exposure to pure ClF_3 at 4.0 psia at up to 300°F. However, as of this writing, the Tenic samples have not been subjected to stress tests or other analyses to evaluate embrittlement or other deterioration.

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Appendix A
BIBLIOGRAPHY OF PERTINENT ARTICLES ON TECHNETIUM

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This listing does not include additional internal reports.

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Appendix B
CALCULATIONS CONCERNING THE REACTION OF CHLORINE
TRIFLUORIDE WITH SATURATED AIR

Appendix B

CALCULATIONS CONCERNING THE REACTION OF CHLORINE TRIFLUORIDE WITH SATURATED AIR

These calculations help address hypothetical hazards associated with a sudden in-leakage of saturated air into a vessel containing chlorine trifluoride at subatmospheric pressure. The principle concern, which is disproven by these calculations, is that the heat of reaction of ClF_3 with the water would be great enough to pose high temperature or high pressure hazards.

Assume that air is saturated with water at 75°F and that the air leaks into a vessel containing pure ClF_3 at an initial pressure of 4 psia until the total pressure increases to 14.7 psia. (Ignore the pressure change due to the reaction at present. Later the assumption will be made that all the water reacts instantaneously with the ClF_3 as a worst case upper limit on the heat and pressure generation).

Saturated vapor pressure of water at $75^\circ\text{F} = 0.43$ psia

Vol of vessel = 4l (the conclusions will be the same regardless of the assumed volume).

Maximum amount of water that could have entered the vessel:

$$4\text{ l} \times (1\text{ gmole}/22.4\text{ l}) \times (18\text{ g H}_2\text{O}/\text{gmole}) \times (492^\circ\text{R}/535^\circ\text{R}) \times (0.43\text{ psia}/14.7\text{ psia}) \times (10.7\text{ psia}/14.7\text{ psia}) \\ = 0.0630\text{ g } (0.0035\text{ gmole H}_2\text{O}, \text{ A very small amount}).$$

Also note that the mole fraction of water to air is:

$$0.43\text{ psia}/14.7\text{ psia} = 0.0292 \text{ or } 2.92\text{ mole \% water in air.}$$

$$\text{Moles of air: } 0.0035\text{ gmole H}_2\text{O}/(0.0292\text{ gmole H}_2\text{O}/\text{air}) = 0.120\text{ gmole air}$$

Amount of ClF_3 present in 4l reactor at 75°F at a pressure of 4 psia:

$$4\text{ l} \times (1\text{ gmole}/22.4\text{ l}) \times (92.4\text{ g ClF}_3/\text{gmole}) \times (492/535) \times (4/14.7) \\ = 4.13\text{ g ClF}_3$$

Amount of ClF_3 reacted by the water inleakage assuming all the water reacts:

$$(0.0630\text{ g H}_2\text{O}/18) \times 92.4 = 0.323\text{ g ClF}_3$$

	2 ClF_3	+	2 H_2O	-	4 HF	+	ClO_2F	+	ClF	$\Delta\text{H} = -81.0$ Kcal/gmole of ClF_3^{A1}
Mass	0.323		0.0630g							
Mol wt	92.4		18							
Moles	0.0035		0.0035							

$$\% \text{ of } \text{ClF}_3 \text{ reacted} = (0.323\text{ g}/4.13\text{ g}) \times 100 = 7.8\%$$

Calculations of rise in temperature of the air that inleaks with the water due to the heat of reaction of ClF_3 and H_2O .

This calculation ignores the heat capacity of the ClF_3 - H_2O by-products and excess ClF_3 and therefore results in a temperature somewhat higher than could possibly occur.

$$\Delta H = 81 \text{ kcal/gmole} \times 0.0035 \text{ gmole } \text{ClF}_3 = 283.5 \text{ cal}$$

Note: The heat-of-reaction for the $\text{ClF}_3/\text{H}_2\text{O}$ reaction as determination by Oliver and Grisard^{A1} does not conform exactly to the present reaction case because Oliver and Grisard made the heat-of-reaction determination by bubbling ClF_3 into water. However, their heat-of-reaction was the only value found and is used here as an approximation.

$$c_p \text{ air} = 7 \text{ cal/(gmole } ^\circ\text{C)}$$

$$\Delta T = [283.5 \text{ cal}/(7 \text{ cal/gmole } ^\circ\text{C})]/(0.120 \text{ gmole of air})$$

$$\Delta T = 337.5^\circ\text{C} \text{ The air temperature could not increase more than } 337.5^\circ\text{C} (639.5^\circ\text{F}).$$

$$\text{Final } T = 379.2^\circ\text{C} (714.5^\circ\text{F})$$

These calculations were done for a 4l reactor but the ratio remains the same for a vessel of any size under the same conditions of pressure and temperature. Therefore

- 1) Maximum T rise = 337.5°C (639.5°F) (Based on heat capacity of the air only)
- 2) Maximum pressure rise of the air = $(1174.5/535) (0.971) (10.7 \text{ psia}) = 22.8 \text{ psia}$
- 3) Maximum percent of ClF_3 reacted = 7.8%

The increase in the moles of gas due to the reaction are not included in the above pressure rise; but since the water is only 2.9 mole percent of the saturated air, this omission has little impact on the final pressure.

Conclusion: Sudden wet air inleakage could not cause an explosion, could not generate sufficient heat to melt steel, or could not generate sufficient pressure to damage the vessel. Since an instantaneous inleakage is a worst case and a gradual inleakage would be much more likely, the heat would be dissipated to the vessel walls and would result in a much lower temperature and pressure rise than the worst case figures calculated here.

The worst expected consequence of sudden inleakage of saturated air into the vessel is that gases would leak from the vessel after the vessel pressure exceeds atmospheric pressure.

^{A1}G. D. Oliver and J. W. Grisard, "Heat of Reaction of Chlorine Trifluoride with Water," K-677, Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, Oak Ridge Gaseous Diffusion Plant, October 1950.

Appendix C
HEAT GENERATION UPON REACTION OF HIGHLY HYDRATED
URANYL FLUORIDE WITH ClF_3

Appendix C
HEAT GENERATION UPON REACTION OF HIGHLY HYDRATED
URANYL FLUORIDE WITH ClF_3

One safety concern for conducting the gas-phase removal of uranium deposits with concentrated ClF_3 is that the ClF_3 may react too rapidly with the deposit thus generating excessive heat to the point that the wall of the containing vessel may weaken or that excessive pressure may be generated. Calculations performed by Safety Engineering and previous lab experiments which reacted pure ClF_3 and uranyl fluoride, suggests that this will not occur. Although the previous lab experiments did not measure the temperature of the uranyl fluoride deposit, the observed generation of UF_6 and depletion of ClF_3 indicated a reaction rate that was too slow to allow generation of excessive heat. The attached calculations show that if all heat generated during the reaction of ClF_3 with $\text{UO}_2\text{F}_2 \cdot 3\text{H}_2\text{O}$ is transferred instantaneously to the by-product gases, the maximum final temperature and pressure would be 1,815°F and 26.1 psig. This pressure is an upper limit which cannot possibly be reached since this figure was derived based on the assumptions of an instantaneous reaction with no heat transfer to the metal reactor walls. The LTLT reactors will likely withstand ~650 psig based on loop stress calculations. The weakest point of the test loop reactor is the AgCl FTIR cell windows, which are contained within the FTIR cabinet.

A set of experiments have been proposed to further support the calculations and previous observations. This set of experiments will involve the following elements.

1. UO_2F_2 will be removed from sections of the same K-33 seal exhaust line that provided sample material for the previous series of experiments. The UO_2F_2 will be packed into a small metal boat around a thermocouple. Then the UO_2F_2 will be subjected to saturated air for sufficient time (perhaps up to one week) to provide a likely "worst case" hydration of the UO_2F_2 sample.
2. The UO_2F_2 contained in the metal boat with the thermocouple will be loaded into the test loop reactor, the reactor flange will be reinstalled, the reactor volume evacuated to low pressure and leak checked, and then pretreatment will begin.
3. The pretreatment gases will consist of ~0.325 psia N_2 and ~0.075 psia of F_2 followed by 0.25 psia of ClF_3 . (The exact concentration may vary). This pretreatment is basically the same pretreatment that will be applied during the gas-phase demonstration to react with moisture or highly reactive deposits prior to administering the full charge of ClF_3 .
4. The result of the pretreatment will be monitored with the FTIR. The system pressure and thermocouple temperature will also be monitored. The depletion of the ClF_3 and generation of HF will be particularly monitored. The gases will be evacuated and the pretreatment repeated as long as the generation of HF exceeds the generation of UF_6 with more than a 4 to 1 mole ratio. (Experimental results may suggest changes to this ratio).
5. Following the pretreatment, the ClF_3 concentration will be slowly increased to 4.0 psia while monitoring the system pressure and the thermocouple temperature. Pure ClF_3 will be added since pure ClF_3 is the most severe test as compared to ClF_3 diluted with nitrogen.
6. Steps 1 through 5 above will first be performed with a small sample of ~2.0g of hydrated UO_2F_2 . The

steps will later be repeated with samples of greater size, i.e. 10g, 20g, (but no greater than 40 g of UO_2F_2). The tests for the larger samples will be modified as dictated by the results for the smaller samples.

REQUIRED CHANGES TO THE EXISTING EXPERIMENTAL EQUIPMENT

The required changes are described below.

1. The present test loop has a total system volume of ~4l which will contain about 4g of ClF_3 at a pressure of 4 psia of pure ClF_3 at 75 °F. A larger volume is required to allow for a large amount of ClF_3 since as much as 40g of UO_2F_2 may be used in a sample. A surge volume of about 36l will be added to increase the total system volume to ~40l. About 40g of ClF_3 can be contained in this volume. The surge volume will have isolation valves to allow it to be isolated if necessary.
2. A metal boat will be equipped with a thermocouple to monitor the temperature of the sample during reaction. The leads from the thermocouple will connect to a "feed through" installed on the reactor flange that can be removed and reinstalled to allow samples to be added to the reactor. The wire insulation is made of Teflon® and the "feed through" is made of solid alumina. These materials are compatible with ClF_3 .

Calculations of the Upper Limit Temperature and Pressure Rise due to Reaction of Chlorine Trifluoride with Hydrated Uranyl Fluoride

Three waters of hydration are assumed for the uranyl fluoride in the equation below as a conservative assumption. The actual degree of hydration is expected to be considerably less. A perfect stoichiometric ratio of reactants is assumed which will tend to maximize the temperature increase. The heat capacities used to calculate the temperature increase of the product gases are based on 25°C as an approximation. Actually the heat capacities increase with temperature, therefore the actual temperature rise will be less than the calculated amount. The reaction produces would partially decompose at high temperature which would tend to increase the final pressure; but considering the conservative nature of the other simplifying assumptions more thorough calculations would not alter the conclusions.

	5ClF ₃	UO ₂ F ₂	3H ₂ O	→	UF ₆	2.5 ClO ₂ F	2.5 ClF	6HF
Mol Wt	92.5	362			352	86.4	54.2	20
Mass (g)	1.25	1.0			0.971	0.596	0.374	0.331
gmols	0.01381	0.00276			0.00276	0.0069	0.0069	0.01656

The heats of formation for the species above are:

ClF ₃ :	-39,000 cal/mole,	Lange's 11 Ed., p. 9-16,
UO ₂ F ₂ • 3H ₂ O:	-604,500 cal/mole,	
UF ₆ :	-505,000 cal/mole,	Lange's 11 Ed., p. 9-16,
ClO ₂ F:	-6,037 cal/mole,	
ClF:	-13,020 cal/mole,	Lange's 11 Ed., p. 9-16,
HF:	-64,800 cal/mole,	Lange's 11 Ed., p. 9-20.

$$\begin{aligned}
 \text{The heat of reaction} &= -505,000 - 2.5 \times 6,037 - 2.5 \times 13,020 - 6(64,800) \\
 &\quad + 5(39,000) + 604,500 \\
 &= -505,000 - 15,092 - 32,550 - 388,800 + 195,000 + 604,500 \\
 &= -141,942 \text{ cal/(gmole UO}_2\text{F}_2 \bullet 3\text{H}_2\text{O)}
 \end{aligned}$$

$$\begin{aligned}
 \text{Heat of reaction per gram of UO}_2\text{F}_2 \bullet 3\text{H}_2\text{O:} \\
 -141,942 \text{ cal/gmole} \times (\text{gmole}/362) = -392.1 \text{ cal/g}
 \end{aligned}$$

Heat capacities of product gases in cal/(g°C):

UF ₆ : C _p	=	0.133	
ClO ₂ F: C _p	=	0.195	
ClF: C _p	=	0.141	Lange, 11 Ed. p.9-16
HF: C _p	=	0.348	Lange, 11 Ed. p. 9-20

Increase in temperature in centigrade of the product gases assuming complete transfer of the heat of reaction to the product gases. (This case represents the maximum temperature increase in the gases):

$$\begin{aligned}
 392.1 \text{ cal/g} &= (0.971 \times 0.133 + 0.596 \times 0.195 + 0.374 \times 0.141 + 0.331 \times 0.348) \times \Delta T \\
 &= (0.129 + 0.116 + 0.053 + 0.115) \times \Delta T \\
 &= 0.413 \times \Delta T \\
 \Delta T &= 949^\circ\text{C} (1,740^\circ\text{F}) \\
 \text{Final} &= \text{Initial} + \Delta T \\
 &= 75^\circ\text{F} + 1,740^\circ\text{F} = 1815^\circ\text{F}
 \end{aligned}$$

Increase in pressure:

Moles of gas increase by a ratio of 12/5

Initial P = 4.0 psia

Final Pressure = 4.0 psia (12/5) (2,275/535)

= 40.8 psia (26.1 psig)

These calculations were done on the basis of one gram of $\text{UO}_2\text{F}_2 \bullet 3\text{H}_2\text{O}$ but the increase in temperature and pressure will remain the same regardless of the amount of $\text{UO}_2\text{F}_2 \bullet 3\text{H}_2\text{O}$ reacted since the amount of by-product gases generated would change proportionally.

APPENDIX D
HEAT GENERATION UPON REACTION OF POWDERED ALUMINUM WITH ClF_3

APPENDIX D

HEAT GENERATION UPON REACTION OF POWDERED ALUMINUM WITH ClF_3

EXPERIMENTAL STEPS

Some locations within cascade equipment could contain metal powder, principally iron and aluminum. Concerns have been expressed regarding the possibility of a runaway reaction between ClF_3 and the powdered metal. An experiment is therefore proposed to evaluate the possibility of an aluminum/ ClF_3 fire initiated by reaction of ClF_3 with moisture within the aluminum powder. These experiments basically model a case in a cascade where powdered metal was formed by corrosive action of the fluorinating gases or powdered aluminum was formed by friction on a malfunctioning aluminum compressor, and moisture inleaked through an opening in the process piping during the years following the cascade shutdown. The process steps for the experiment basically follow the proposed process steps for gas-phase decontamination of process equipment. These steps should preclude the possibility of a rapid reaction of the aluminum with ClF_3 .

1. The aluminum powder will be packed into a small metal boat around a thermocouple. Enough aluminum will be added to adequately cover the thermocouple. Then the powder will be subjected to saturated air to simulate possible moisture conditions in a portion of the cascade that was previously exposed to the atmosphere.
2. The boat, powder, and thermocouple will be loaded into the test loop reactor, the reactor flange will be reinstalled, the reactor volume evacuated to low pressure and leak checked, and then pretreatment will begin.
3. The pretreatment gases will consist of ~ 0.325 psia N_2 and ~ 0.075 psia of F_2 followed by 0.25 psia of ClF_3 . (The exact concentration may vary if called for by future program plans).
4. The thermocouple readings of the aluminum temperature and the system temperature will be observed. The maximum temperature of the aluminum and corresponding ClF_3 partial pressure will be especially noted. The pretreatment gases will be evacuated and the pretreatment repeated as often as necessary if the ClF_3 is depleted with a corresponding generation of HF. The expectation is that the pretreatment will dry the moisture from the aluminum and form an AlF_3 film on the aluminum powder which will preclude the possibility of a rapid reaction during the additional of pure ClF_3 described in step 5.
5. Following the pretreatment, the ClF_3 concentration will be slowly increased while monitoring the system pressure and the thermocouple temperature. The maximum amount of ClF_3 contained in the loop during these experiments will be $\sim 4\text{g}$, since the surge volume will not be used during this evaluation and will be valved out of the loop. The 4g of ClF_3 corresponds to a partial pressure of 4.0 psia of ClF_3 . (Since the surge volume has not been installed at the time of this writing, it may not be present when the ClF_3/Al tests are done). If the thermocouple reading indicates a rapid reaction is occurring, no additional ClF_3 will be added. A highly exothermic reaction of ClF_3 and aluminum, if it occurred, is expected to result in a rapid decrease in pressure rather than an increase in pressure in spite of the rapid temperature increase because of the formation of solid AlCl_3 and AlF_3 . (A rapid decrease in pressure was observed during an actual ClF_3 /Aluminum fire that previously occurred in operating gaseous diffusion equipment). The reaction equation is as follows:

The attached calculations approximate the temperature increase in a 1-in section of the reactor at ~1400°F if all of the ClF₃ were to burn with the aluminum. Assuming the initial reactor temperature is 75°F, the final temperature is estimated at ~1475°F, which is well below the melting point of nickel at 2,150°F.

REQUIRED CHANGES TO THE EXISTING EXPERIMENTAL EQUIPMENT

One required change will be the thermocouple and its connections to allow monitoring the temperature of the aluminum sample. The thermocouple connection and a description of how it passes through the reactor is given in Appendix C. Also, as commented in the attached calculations, the temperature generated could exceed the melting point of the nickel reactor wall if the ClF₃/Al reaction occurred too rapidly for heat to transfer from the small area of the reaction site. For this reason, a thick piece of nickel will be placed in the bottom of the reactor to allow additional time for heat transfer.

Calculations for the Approximate Upper Limit Temperature Rise due to Reaction of Chlorine Trifluoride with Powdered Aluminum during Laboratory Experiments

The following equation is assumed for the reaction of ClF₃ with aluminum:

The AlCl₃ is a solid at room temperature, but is vaporized at high temperature; therefore, the AlCl₃ would transport some heat away from the reaction site and tend to cool to reaction site. For the approximate calculations below, this effect is ignored.

	<u>ClF₃</u>	<u>Al</u>
Mass (g)	4.0	1.56
Mol wt	92.4	26.98
Moles	0.0433	0.0577

$\Delta H_f \text{ ClF}_3$	=	-39 kcal/gmole
$\Delta H_f \text{ AlCl}_3$	=	-166.2 kcal/gmole
$\Delta H_f \text{ AlF}_3$	=	-311 kcal/gmole
ΔH_r	=	$3(-311) + (-166.2) - 3(-39) = -982.2 \text{ kcal}$

Therefore, the heat of reaction on the basis of the ClF₃ present is:

$$-982.2 \text{ kcal}/3 = 327.4 \text{ kcal/gmole of ClF}_3$$

The following calculation shows that if the 4g of ClF₃ burns with the aluminum, 56.2 Btu of heat are evolved.

Heat generated per 4.0g of ClF₃:

$$\begin{aligned} 4.0\text{g}/92.4 &= 0.0433 \text{ gmole ClF}_3 \\ 0.0433 \text{ gmole} (327,400 \text{ cal/gmole})(0.003968 \text{ Btu/cal}) & \\ &= 56.2 \text{ Btu} \end{aligned}$$

Properties of 2-in, Sch. 80 nickel pipe (the reactor is made of this pipe):

ρ	=	0.275 lb/in ³ (density of nickel)
specific heat	=	0.11 Btu/lb °F
melting point	=	2150 °F
wall thickness	=	0.218 inch
ID	=	1.939 in

Mass of a 1-in. section:

$$\begin{aligned} \text{Mass} &= \text{volume} \times \text{density} \sim 2\pi r \times \text{thickness} \times \text{length} \times 0.275/\text{in}^3 \\ &= 2\pi (1.939 \text{ in}/2) \times 0.218 \text{ in} \times 1.0 \text{ in} \times 0.275 \text{ lb/in}^3 \\ &= 0.365 \text{ lb} \end{aligned}$$

Temperature rise if the 56.2 Btu is evenly distributed along a 1-in section of the reactor (a simplifying approximation).

$$\begin{aligned} \Delta T &= 56.2 \text{ Btu}/(0.11 \text{ Btu/lb °F} \times 0.365 \text{ lb}) \\ &= 1400 \text{ °F} \end{aligned}$$

The heat transferred to the reaction products, excess aluminum, and reaction boat is ignored since the mass of these items is small compared to that of the pipe. The heat transferred to portions of the reactor outside of the assumed 1-in section is also ignored. The temperature rise would have been less if loss of heat to these areas was considered. The 1400°F temperature rise compares to the melting point of nickel at 2150°F.

If the ClF_3 were to react with the aluminum very rapidly, the heat evolved may be concentrated in an area small enough to cause a temperature rise that could melt the nickel. Therefore, a thick piece of nickel or other suitable material will be placed in the bottom of the reactor as added protection.

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