ORNL/TM-13403

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Laboratory Tests Using Chlorine Trifluoride in Support of Deposit Removal at MSRE

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Chemical Technology Division

LABORATORY TESTS USING CHLORINE TRIFLUORIDE
IN SUPPORT OF DEPOSIT REMOVAL AT MSRE

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Date Published — April 1997

Prepared by the
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managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464

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EXECUTIVE SUMMARY

This investigation complements a previous Chemical Technology Division study (ORNL/TM-13191) on treatment of the reactive gases present in the Molten Salt Reactor Experiment (MSRE) off-gas system. This work addresses the performance of the Reactive Gas Removal System trapping materials with chlorine trifluoride (ClF_3) and the potential for generating halogen oxides in the off-gas. The basic performance of the alumina/molecular sieve system with ClF_3 is essentially equivalent to that seen during fluorine trapping operations. Temperatures and fluorine loadings are not significantly different from those seen during tests with F_2 . For operations with significant levels of ClF_3 (such that a hot reaction front is established), a very small amount of chlorine dioxide (ClO_2) escapes the alumina column during a short period of time. Only upon breakthrough of the alumina column are significant levels of halogen oxides detected. At low ClF_3 flows (those that do not establish a hot reaction front), perchloryl fluoride (ClO_3F) is generated during much of the trapping operation and, as before, a very small amount of ClO_2 is detected for a short period. Breakthrough is again accompanied by significant generation of halogen oxides. The only significant product seen before breakthrough is ClO_3F – a rather unreactive and innocuous gas.

Only a limited amount of information was obtained about the retention of gases on the trapping media. It appears that the capacity and affinity of the molecular sieve are such that very little halogen oxide will be seen in the effluent from the second column during normal operation. No halogen oxides were detected after the low-flow trial during extensive purging of both columns with helium. Upon evacuation of the molecular sieve column and cold trapping of the exhaust, low levels of halogen oxides were recovered (< 20 std cc). Evacuation and cold trapping of the alumina column were inconclusive, but we expect a low level of sorption on the spent alumina. Furthermore, this level should diminish with an increasing temperature in the alumina reaction front.

After treatment of irradiated MSRE simulant salt with 0.5 atm of ClF_3 for 18 h, temperature and weight measurements, plenum gas infrared spectra, and visual inspection all indicated that the salt is basically inert to this level of ClF_3 exposure.

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ABSTRACT

Experimental trials were conducted to investigate some unresolved issues regarding the use of chlorine trifluoride (ClF_3) for removal of uranium-bearing deposits in the Molten Salt Reactor Experiment (MSRE) off-gas system. The safety and effectiveness of operation of the fixed-bed trapping system for removal of reactive gases were the primary focus. The chief uncertainty concerns the fate of chlorine in the system and the potential for forming explosive chlorine oxides (primarily chlorine dioxide) in the trapping operation. Tests at the MSRE Reactive Gas Removal System reference conditions and at conditions of low ClF_3 flow showed that only very minor quantities of reactive halogen oxides were produced before column breakthrough. Somewhat larger quantities accompanied breakthrough. A separate test that exposed irradiated MSRE simulant salt to ClF_3 confirmed our expectation that the salt is basically inert for brief exposures to ClF_3 at room temperature.

1. INTRODUCTION

This work is motivated by the need to ensure safe and effective use of chlorine trifluoride (ClF_3) as a fluorinating agent for removal of uranium-bearing deposits in the Molten Salt Reactor Experiment (MSRE) off-gas system. The need to use a powerful fluorinating agent, such as ClF_3 , for deposit removal was demonstrated by the inability to remove the existing MSRE off-gas deposits by vacuum sublimation. It was concluded that the uranium-bearing plugs could not be pure UF_6 . Instead, they probably contained hydrolyzed material (e.g., hydrous UO_2F_2) that resulted from moisture intrusion or reduced uranium fluorides (e.g., UF_4/UF_5) that resulted from the self-induced radiolysis of UF_6 deposits.

The primary focus for this laboratory testing is the disposal of excess ClF_3 in the existing two-stage alumina/molecular sieve fixed-bed traps. Previous studies [1] have shown that alumina is an effective trapping agent for the fluorine content of ClF_3 but that most of the chlorine passes through this trap. Although a number of studies have investigated the reaction of ClF_3 with various materials, none of them provide a basis for predicting the outcome in the alumina bed [2-6]. Reaction of ClF_3 with oxide surfaces

can produce many different halogen oxides depending upon the temperature, moisture level, residence time, ClF_3 concentration, and specific reactivity of the solid. The behavior in a fixed-bed column is further complicated by sorption effects in the downstream packing. The complicated decomposition mechanism of one of the halogen oxides, chlorine dioxide (ClO_2), adds yet another variable to be accounted for [7].

Because of these uncertainties and the fact that the potential exists to produce explosive halogen oxides (e.g., ClO_2), this brief experimental test program was initiated. Some of the same reaction products that occur in the alumina trap will occur in the MSRE off-gas piping to a much lesser (and indeterminate) extent. However, our focus on the trapping operation is appropriate because it has by far the greatest potential for generation of explosive gases.

2. EXPERIMENTAL

2.1 TRAPPING OF ClF_3

2.1.1 Materials and Equipment

Materials

The trapping materials used for this work, listed in Table 1, are identical to those used in a previous study [8] and are those presently in use in the MSRE Reactive Gas Removal System (RGRS). For the high-flow trial, full columns of alumina (48.1 g of Al_2O_3) and molecular sieve (42.5 g of 13X pellets) were used. For the low-flow trial, only a one-third charge of packing was used (16.0 g of Al_2O_3 , 14.2 g of molecular sieve). The compressed gases used for these tests were ultra-high-purity helium (Air Liquide America Corp.) and research-grade ClF_3 (Air Products and Chemicals, Inc.). Neither feed gas had significant levels of infrared-active impurities. Potassium hydroxide (1 M) was used for the final scrubbing of the exhaust gas.

Table 1. Materials and equipment used in ClF_3 trapping tests

Item	Description
Materials ^a	
Alumina	LaRoche Chemicals A-201 5 × 8 mesh, spherical
Molecular sieve	Linde 13X, 1/8-in.-diam cylindrical pellets
Equipment ^{b, c}	
Alumina column	0.75-in.-OD × 0.035-in.-wall 304L SS tube, 1 ft long
Molecular sieve column	0.75-in.-OD × 0.035-in.-wall 304L SS tube, 1 ft long
ClF_3 flow controller	Tylan 2900M mass-flow controller, 100 sccm F_2 (full scale)
He flow controller	MKS mass-flow controller type 1459C01667185, 1000 sccm N_2 (full scale)
FTIR flow cell	10-cm path, 39-mm-ID ZnSe windows
FTIR instrument	Bomem MB-104 with ZnSe internal optics
Data logging ^b	
Temperature and flows	Automatic with Validyne UPC601-T card and Easy Sense v2.01 DOS program on IBM-386 PC
FTIR spectra	Manually every 5 min using WinBomemEasy software on IBM-486 PC

^aSame materials and preparation used in previous tests and now being used at the Molten Salt Reactor Experiment.

^b FTIR = Fourier transform infrared.

^c sccm = standard cubic centimeters per minute.

Equipment

The experimental equipment consisted of auxiliary piping, vessels, and instruments integrated with an existing reactive-gas manifold. This system is depicted in Fig. 1, and the significant equipment items are identified in Table 1. All of the piping in the system is monel tubing, except for the 304L SS fixed-bed columns. Much of the manifold was not necessary for the actual flow test; however, it was essential for preparation of the system, troubleshooting during operation, and disposal/analysis of excess reactive gases.

Not shown in Fig. 1 are the thermocouples used to monitor the wall temperatures of the alumina and molecular sieve columns. For the alumina column, wall temperatures were measured at the entrance, middle, and exit of the column. Only the wall temperature at the entrance to the molecular sieve column was measured. In order to obtain representative wall temperatures, 1/16-in.-diam Type K thermocouples were firmly clamped to the column wall and then insulated in the vicinity of the tip of the thermocouple. For the high-flow trial, the entrance and exit thermocouples were located 1 in. from the ends of the bed; for the low-flow trial, they were located as close as possible to the actual bed entrance and exit. The middle thermocouple was always located equidistant from the ends of the bed. Another minor feature not shown in Fig. 1 is the heat tracing of piping between the two columns. A 1-ft section of monel tubing (6-in. length of 1/4-in. tubing followed by 6-in. length of 1/2-in. tubing) connecting the two columns was heated to 100°C in order to approximate the gas residence time in the heat-traced line that exists in the RGRS.

2.1.2 Test Method

Use of a scaled-down fixed bed operated at the reference superficial velocity of feed constituents to predict full-scale performance is a widely accepted practice and was successfully used in a previous study of fluorine trapping [8]. The beginning of a trial was established by introduction of ClF_3 to a flowing helium stream. Both columns were operated upflow, as shown in Fig. 1, but the flow bypassed the molecular sieve column during periods when the alumina exhaust was ported to the Fourier transform infrared (FTIR) spectroscopy flow cell. This limitation was not significant, and all of our

Fig. 1. Diagram of the experimental system for fixed-bed trapping.

experimental goals were met with this manner of operation. Because we had only one FTIR instrument, choices had to be made about which column's exhaust gases would be monitored during a particular period of the trial. In general, we adopted the approach of monitoring the exhaust from the alumina column until an infrared-active species appeared and established a semblance of steady behavior. During the second trial at low ClF_3 flows, we intentionally ported more gas to the molecular sieve column to assess the ability of the second column to load and retain halogen oxides. Reference spectra on an evacuated or helium-filled cell were taken at the beginning and end of each trial. All spectra were taken with a 450–4400 cm^{-1} wavenumber range (1- cm^{-1} resolution), and five averaged scans were taken at a rate of six scans/minute for each measurement. For both trials there were no significant flow restrictions and the system pressure was just slightly above atmospheric pressure due to the hydrostatic pressure (~0.9 psi) associated with the caustic scrubbers.

2.2 EXPOSURE OF IRRADIATED SALT TO ClF_3

2.2.1 Materials and Equipment

The materials and equipment for this batch exposure test consisted of a 1/2-in.-OD $\times$ 0.035-in.-wall $\times$ 4-in.-long monel tube capsule connected to the existing manifold/FTIR setup shown in Fig. 1. The open end of the capsule was sealed by compression fittings and an all-metal valve (monel internals). This assembly, along with the manifold and optical cell, was preconditioned with 0.5 atm of ClF_3 to passivate all surfaces. The capsule was pumped out to high vacuum, backfilled with helium, and transferred to an inert-gas glove box for loading with irradiated MSRE simulant salt. In the glove box 0.98 g of powdered MSR-2 simulant salt (~2% fluorine deficient, final High Flux Isotope Reactor cooling pool discharge on July 19, 1996) was loaded into the open capsule, the capsule was reassembled, and the contents were isolated by closing the attached valve. After connecting the capsule to the manifold, a thermocouple was clamped to the bottom of the tube and the entire capsule was insulated with a 3-in.-thick layer of fiberglass insulation.

2.2.2 Test Method

Part of the test involved measuring the infrared bands that we would expect to see in the absence of salt exposure, that is, those features associated with the reaction of ClF_3 with the piping and equipment ("passivation"). Representative "passivation" spectra were obtained in the course of preconditioning the system and during charging of the capsule with ClF_3 . The same FTIR instrumental parameters used during the trapping trials were used for this test.

3. RESULTS

3.1 TRAPPING RESULTS

The results consist of measurements of the wall temperatures, infrared spectra, and breakthrough behavior during the trapping of ClF_3 on the scaled-down packed beds assembled for this study. Two trials were conducted with the same total superficial gas velocity ($v_{\text{total}} = 40 \text{ cm/min}$), but one trial was conducted with a high ClF_3 flow and the other had a low ClF_3 flow. The trial at high ClF_3 flow (49% ClF_3 / 51% He) was similar in character to the RGRS trap limit of 1000 sccm of F_2 established in a previous study [8]. The second trial, at low ClF_3 flow, used a 5% ClF_3 / 95% He mixture. The major results from these two tests are summarized in Table 2, and the detailed temperature and flow profiles are displayed in Figs. 2 and 3. The erratic pattern of the temperature measured at the alumina bed exit during the high-flow trial was due to a thermocouple failure. The exit temperature profile should resemble a reflection of the entrance profile, as was seen in previous work [8].

Table 2. Summary of fixed-bed trapping parameters and performance

Bed length (in.)	ClF_3 flow (sccm)	He flow (sccm)	ClF_3 molar flux ($\text{mol/m}^2 \cdot \text{s}$)	Peak wall temp ($^{\circ}\text{C}$)	Peak $[\text{ClO}_2]$ detected (torr) ^a	F loading at breakthrough (g F/ g Al_2O_3)
12	48.	50	0.15	210	2.3	0.48
4	4.8	95	0.015	40	13.4	0.135

^aBased upon a provisional conservative estimate of the peak extinction associated with the low-resolution measurement of the 1109-cm^{-1} band of 300 torr-cm per absorbance unit. See Appendix B.

The temperatures and fluorine loading established in the high-flow trial are quite close to the values found in previous studies with fluorine [1, 8] and ClF_3 [1]. The lower temperature and decreased loading of fluorine on alumina for the low-flow trial were expected and were also found in previous studies for conditions which did not establish a hot reaction front [1]. It is interesting to note that the heating of the molecular sieve by reaction with ClF_3 is similar in magnitude to that seen with alumina.

Fig. 2. Wall temperatures and flows during high-flow trial.

Fig. 3. Wall temperatures and flows during low-flow trial.

In this section only a summary of the infrared (FTIR) spectroscopy results is presented – a complete display of the spectra is included in Appendix A. The most important FTIR results concern the generation of halogen oxide gases during trapping of ClF_3 on alumina. In Figs. 4–6, representative spectra of the predominant halogen oxide species (ClO_2 , ClO_2F , ClO_3F) are displayed. These spectra reveal that there are ample features to establish the identity and concentration of each halogen oxide without resorting to extensive deconvolution. The only potential complication, the overlap of the 1109-cm^{-1} ClO_2 band and the 1106-cm^{-1} ClO_2F band, did not present itself because these species did not appear together. This is likely to be the case in systems such as this one that have either a deficiency or an overabundance of fluorinating agent, since ClO_2 is rapidly converted to ClO_2F by fluorine or ClF_3 [9]. Nominal concentrations were calculated from estimates (see Appendix B) of the extinction coefficients of these bands.

Fig. 4. Representative ClO_3F infrared spectrum (spectrum no. 11 from low-flow trial).

Fig. 5. Representative ClO_2 infrared spectrum (spectrum no. 18 from high-flow trial).

Fig. 6. Representative ClO_2F infrared spectrum (spectrum no. 25 from high-flow trial). Note: minor level of ClO_3F is also present.

The evolution of infrared-active species in the exhaust gas from the alumina column is shown in Figs. 7 and 8. In these figures each ordinate in the stack of spectra is independently scaled to show maximum detail (i.e., peak heights should not be compared across the stack). The quantitative results associated with these features are summarized in Figs. 9 and 10. For the high-flow trial a small amount of ClO_2 (~ 2 torr) was detected in the exhaust from the alumina column 40 min prior to column breakthrough. This gas could have been present only for a short period of time (< 17 min). The measured ClO_2 level was somewhat higher during the low-flow trial (~ 15 torr) and occurred about 90 min prior to column breakthrough. As in the previous trial, the gas was present for only a very short period of time (~ 14 min). For both trials an increasing level of halogen oxides (primarily ClO_3F and ClO_2F) and HF accompanied the ClF_3 breakthrough of the alumina bed. For the high-flow trial this increase is with respect to an infrared-transparent exhaust gas (i.e., no halogen oxides), while for the low-flow trial this increase is superimposed upon a relatively constant generation of ClO_3F .

The FTIR results discussed previously and displayed in Figs. 9 and 10 all refer to detection directly downstream from the alumina column. No infrared-active species were seen in the exhaust gas from the molecular sieve column during the low-flow trial, even after extensive purging with helium. After the low-flow trial, small amounts of halogen oxides (< 20 std cc) were recovered from the molecular sieve by pumping down the column to high vacuum and cold trapping the exhaust. The spectrum from expansion of the cold trap contents (after warming to room temperature) is shown in Fig. 11, and estimates of the amount of recovered gases are summarized in Table 3. In addition to the species identified in Table 3, SiF_4 , CO_2 , and very small amounts of gas with absorption bands at 849, 887, 1270, and 1504 cm^{-1} are present in the recovered sample. These "unidentified" peaks are all consistent with the reported spectrum of SO_2F_2 [9]. The source of sulfur in the system is not known. Recovery of material sorbed on the alumina column after the low-flow trial was also attempted, but the results were inconclusive because of leakage of ClF_3 into this sample from the supply piping.

These results indicate that the basic performance (i.e., loadings, temperatures) of the alumina bed with ClF_3 is very similar to that with fluorine. The major difference between the two – the potential for generation of halogen oxide gases with ClF_3 – is virtually a nonissue for standard operation with flows of ClF_3 that establish a hot reaction front. A very minor amount of ClO_2 was detected for only a short period of time. The only other generation of halogen oxide gases was associated with column breakthrough. For the case of a cold reaction front (i.e., low ClF_3/F_2 flows), more halogen oxides are formed; however, the dominant species is perchloryl fluoride (ClO_3F), a relatively stable compound.

Fig. 7. Evolution of halogen oxide infrared peaks during high-flow trial.

Fig. 8. Evolution of halogen oxide infrared peaks during low-flow trial.

Fig. 9. Gas concentrations measured downstream of the alumina trap during high-flow trial.

Fig. 10. Gas concentrations measured downstream of the alumina trap during low-flow trial.

Fig. 11. Halogen oxide gases recovered from evacuation of molecular sieve after low-flow trial.

Table 3. Estimated amount of gases recovered from evacuation of molecular sieve after the low-flow trial

Final expanded volume: ~ 600 cc

Component	Wavenumber (cm ⁻¹)	Peak absorbance	Estimated amount (std cc)
ClO ₃ F	716	0.88	3.1
ClO ₂	1109	0.48	11.4 ^a
ClO ₂ F	1272	0.20	1.4
Total			15.9

^aBased upon a provisional conservative estimate of the peak extinction associated with the low-resolution measurement of the 1109-cm⁻¹ band of 300 torr-cm per absorbance unit. See Appendix B.

3.2 RESULTS FROM EXPOSURE OF IRRADIATED SALT TO ClF₃

After pumping down the salt sample to a high vacuum, 0.5 atm of ClF₃ was admitted to the capsule and optical cell, and the system was then isolated by valves. No rise in outer-wall temperature was detected at the bottom of the capsule. The exposure of the salt was continued for 18 h before the first gas sample was expanded from the capsule to the optical cell (from ~10 cc to ~120 cc, or an expansion factor of 13). Comparison of the passivation spectrum with the sample gas spectrum in Fig. 12 reveals that all features present in the gas sample are also present in the passivation gas. In Fig. 13 a more detailed look at the region near the strongest UF₆ absorption band (625 cm⁻¹) shows that only the 630-cm⁻¹ bands of ClO₂F are present in this region. No change in sample weight was measured after capsule evacuation, helium backfill, and unloading in the inert glove box.

Fig. 12. Infrared spectra from ClF_3 passivation and from exposure of irradiated salt to ClF_3 .

Fig. 13. Infrared spectra from ClF_3 passivation and from exposure of irradiated salt to ClF_3 : 625- cm^{-1} region.

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Appendix A
COMPLETE FTIR RESULTS

Table A.1 and Figs. A.1–A.10 provide complete documentation of the FTIR results from this study. Because of minor deposition on and degradation of the ZnSe optical windows (evident as rounded “window bands”) and slight variations in the moisture and CO₂ levels in the optical path, some of the spectra are referenced (by spectral subtraction) to a featureless spectrum taken during the actual trial rather than to the initial reference spectrum. This subtraction is indicated in the following table, and the subtrahend spectrum is available for inspection in the graphs. This normalization greatly improves the clarity of the results. Note also that the growth and decay of absorbance bands are influenced by the dilution and backmixing introduced by the piping and infrared cell volume. These downstream volumes broaden the concentration history of the species that escape the alumina column. This effect is especially evident when the flow path is switched from analysis of one column's exhaust to the other.

Special comments need to be made about the spectra after breakthrough of the alumina column during the high-flow trial (nos. 28–39). The features in these spectra are primarily from SiF₄ (1030-cm⁻¹ line) and ClO₃F. Silicon tetrafluoride is an expected product from reaction of the molecular sieve (an aluminosilicate) with ClF₃, and ClO₃F is one of the other predominant reaction products at low temperatures. However, the fact that these species are seen in the exhaust gas of the high-flow trial but not of the low-flow trial needs some explanation. The molecular sieve used for the high-flow trial had seen some slight use in a previous trial with ClF₃ and may have had some sorbed species on the packing near the exit. The molecular sieve used in the low-flow trial had not seen previous exposure to ClF₃ or exhaust gases. The molecular sieve from both trials experienced about 0.4 h of feed flow after the breakthrough of the alumina column. Therefore, the molecular sieve charge from the high-flow trial reacted with ten times the amount of ClF₃ seen by the molecular sieve of the low-flow trial. This more extensive reaction accounts for the species detected in the exhaust gas during the high-flow trial. In any event, the exhaust species seen in spectra nos. 28–49 of the high-flow trial are due to reaction of the molecular sieve with ClF₃ after breakthrough of the alumina column. If the alumina column is not operated past breakthrough, we expect to see very few infrared-active species in the exhaust gas of the molecular sieve column.

Table A.1. Identification of FTIR spectra

Spectrum no.	Elapsed time (h)	Sampling details ^a
High-flow trapping		
1	0.00	Alumina effluent, started ClF ₃ flow
2	0.08	Alumina effluent
3	0.22	Alumina effluent
4	0.27	Alumina effluent
5	0.28	Alumina effluent
6	0.32	Alumina effluent
7	0.37	Alumina effluent
8	0.40	Alumina effluent
9	0.55	Alumina effluent
10	0.72	Alumina effluent
11	0.87	Alumina effluent
12	1.05	Alumina effluent
13	1.32	Alumina effluent
14	1.57	Alumina effluent
15	1.77	Alumina effluent
16	2.02	Alumina effluent
17	2.17	Alumina effluent (– no. 16)
18	2.37	Alumina effluent (– no. 17)
19	2.45	Alumina effluent (– no. 17)
20	2.50	Alumina effluent (– no. 17)
21	2.67	Alumina effluent (– no. 17)
22	2.77	Alumina effluent (– no. 21)
23	2.85	Alumina effluent (– no. 21)
24	2.92	Alumina effluent (– no. 21)
25	2.97	Alumina effluent (– no. 21)
26	3.08	Molecular sieve effluent (– no. 21)
27	3.13	Molecular sieve effluent
28	3.20	Molecular sieve effluent
29	3.25	Molecular sieve effluent
30	3.30	Molecular sieve effluent
31	3.37	Molecular sieve effluent
32	3.45	Molecular sieve effluent, stopped ClF ₃ , increased to 500 sccm He
33	3.50	Molecular sieve effluent
34	3.57	Molecular sieve effluent
35	3.62	Molecular sieve effluent
36	3.65	Molecular sieve effluent
37	3.68	Molecular sieve effluent
38	3.75	Molecular sieve effluent
39	3.78	Molecular sieve effluent

Table A.1 (continued)

Spectrum no.	Elapsed time (h)	Sampling details ^a
Low-flow trapping		
1	0.00	Alumina effluent, started ClF ₃ flow
2	0.05	Alumina effluent
3	0.12	Alumina effluent
4	0.18	Alumina effluent
5	0.28	Alumina effluent
6	0.43	Alumina effluent
7	0.50	Alumina effluent
8	0.53	Molecular sieve effluent
9	0.58	Molecular sieve effluent
10	0.65	Molecular sieve effluent
11	0.70	Molecular sieve effluent
12	0.73	Alumina effluent (– no. 11)
13	0.85	Alumina effluent (– no. 11)
14	0.92	Alumina effluent (– no. 11)
15	1.00	Alumina effluent (– no. 11)
16	1.03	Molecular sieve effluent (– no. 11)
17	1.07	Molecular sieve effluent (– no. 11)
18	1.12	Molecular sieve effluent (– no. 11)
19	1.28	Molecular sieve effluent
20	1.45	Molecular sieve effluent (– no. 19)
21	1.50	Alumina effluent (– no. 20)
22	1.55	Alumina effluent (– no. 20)
23	1.60	Alumina effluent (– no. 20)
24	1.63	Alumina effluent (– no. 20)
25	1.68	Alumina effluent (– no. 20)
26	1.73	Alumina effluent (– no. 20)
27	1.82	Molecular sieve effluent (– no. 20)
28	1.87	Molecular sieve effluent
29	1.90	Molecular sieve effluent
30	2.00	Molecular sieve effluent
31	2.05	Alumina effluent (– no. 30)
32	2.10	Molecular sieve effluent (– no. 30)
33	2.15	Molecular sieve effluent
34	2.20	Molecular sieve effluent
35	2.32	Molecular sieve effluent
36	2.42	Molecular sieve effluent
37	2.57	Molecular sieve effluent
38	2.73	Molecular sieve effluent (– no. 37)
39	2.83	Alumina effluent (– no. 38)
40	2.90	Alumina effluent (– no. 38)
41	2.97	Molecular sieve effluent (– no. 38)
42	3.02	Molecular sieve effluent
43	3.08	Molecular sieve effluent

Table A.1 (continued)

Spectrum no.	Elapsed time (h)	Sampling details ^a
44	3.27	Molecular sieve effluent, stopped ClF ₃ , maintained 95 sccm He
45	3.48	Molecular sieve effluent
46	3.63	Molecular sieve effluent
47	3.80	Molecular sieve effluent
48	4.17	Molecular sieve effluent
49	4.55	Molecular sieve effluent

^aSpectral subtraction is indicated in parentheses.

Fig. A.1. Spectra from high-flow trapping, nos. 1–10 (elapsed time from 0 to 0.72 h).

Fig. A.2. Spectra from high-flow trapping, nos. 11–20 (elapsed time from 0.87 to 2.5 h).

Fig. A.3. Spectra from high-flow trapping, nos. 21-24 (elapsed time from 2.67 to 2.92 h).

Fig. A.4. Spectra from high-flow trapping, nos. 25–30 (elapsed time from 2.97 to 3.3 h).

Fig. A.5. Spectra from high-flow trapping, nos. 31-39 (elapsed time from 3.37 to 3.78 h).

Fig. A.6. Spectra from low-flow trapping, nos. 1–11 (elapsed time from 0 to 0.7 h).

Fig. A.7. Spectra from low-flow trapping, nos. 12-20 (elapsed time from 0.73 to 1.45 h).

Fig. A.8. Spectra from low-flow trapping, nos. 21–30 (elapsed time from 1.5 to 2.0 h).

Fig. A.9. Spectra from low-flow trapping, nos. 31-40 (elapsed time from 2.05 to 2.90 h).

Fig. A.10. Spectra from low-flow trapping, nos. 41-49 (elapsed time from 2.97 to 4.55 h).

Appendix B

EXTINCTION COEFFICIENTS USED IN THIS STUDY

The general approach for estimating halogen oxide concentrations from the FTIR absorbance bands was to draw upon the most consistent set of extinction coefficients available in the literature. Relying on this type of estimation is not the most accurate method, and it is clear that the use of calibration gases would give more precise answers. However, the limitations of this work and the inherent instability of many of the halogen oxides argue for the more pragmatic approach adopted in this study. In Table B.1, all extinction coefficients, ϵ (absorbance = concentration [torr] • path [cm] • ϵ) are based upon the maximum peak height of a particular feature, and the "recommended" values were used to report concentrations in this study. In situations where more than one infrared feature was available for prediction, the feature with the least interference was used (generally 1109 cm^{-1} for ClO_2 , 1272 cm^{-1} for ClO_2F , and 1317 cm^{-1} for ClO_3F). Except for ClO_2 , the extinction coefficients from various sources in the table show reasonable agreement. The inherent instability of ClO_2 and the potential for ClO_2F interference (in some studies) are the likely sources of this lack of consensus in the literature. The 854 reciprocal extinction value for ClO_2 in Table B.1 is almost certainly in error (too weak a line predicted) and is not in concert with the extinction values for the other asymmetric Cl-O stretches of the halogen oxides. We have adopted a value of 300 torr-cm per absorbance unit for the reciprocal extinction of the 1109- cm^{-1} line of ClO_2 as a conservative upper limit. It should be noted that a detailed and reliable high-resolution FTIR study of ClO_2 has recently been conducted, but these results are not readily translated to low-resolution applications [Ortigoso, J., et al., *J. Mol. Spectros.* **156**, 89-97 (1992)]. In this study the weaker infrared features of ClO_2 located at 944 and 2041 cm^{-1} were documented, and integrated intensities of the high-resolution features of the primary absorption bands were reported.

Table B.1. Summary of relevant extinction coefficients

Gas	Wavenumber (cm ⁻¹)	References ^a	Reciprocal extinction coeff. (torr-cm per absorbance)	Relative line intensity, % (literature)	Relative line intensity, % (this study)	Recommended reciprocal extinction coeff. (torr-cm per absorbance)
ClO ₃ F	716	E. A.Smith [1]	66.4	30.1	65	45
		A. Engelbrecht [2]	57.7	49.6		
		K-25 [3]	45.0	76.0		
	1062	E. A.Smith [1]	115	17.4	27	115
		A. Engelbrecht [2]	115	24.9		
	1317	E. A.Smith [1]	20.0	100	100	34.2
		A. Engelbrecht [2]	28.6	100		
		K-25 [3]	34.2	100		
	ClO ₂ F	1106	E. A.Smith [1]	123	35.6	55
A. J. Arvia [4]			238	40.6		
K-25 [3]			240	36.5		
1272		E. A.Smith [1]	43.8	100	100	87.6
		A. J. Arvia [4]	96.8	100		
		K-25 [3]	87.6	100		
ClO ₂	1109	E. A.Smith [1]	854	—		300
		A. H. Nielsen [5]	185	—		
ClF ₃	760	K-25 [3]	468	—		468
HF	4039	K-25 [3]	558	—		558

^aReferences: [1] Smith, E. A., et al., *Infrared Spectra of ClO₂, ClO₂F and ClO₃F*, GAT-T-687, Goodyear Atomic Corp., Portsmouth, Ohio (October 1959); [2] Engelbrecht, A., et al., *J. Inorg. Nucl. Chem.* 2, 348 (1956); [3] K-25 local reference from Schwab and Farrar, updated by L. D. Trowbridge; [4] Arvia, A. J., et al., *Spectrochim. Acta* 19, 1449 (1963); [5] Nielsen, A. H. et al., *J. Chem. Phys.* 20, 1878 (1952).

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