MARTIN MARIETTA

ER036111

ER DMC Central

K/TCD-1116

The Stability of ClO_2 as a Product of Gas Phase Decontamination Treatments

D. W. Simmons
Technical Division

September 1994

CAUTION

This document has not been given final patent clearance and is for internal use only. If this document is to be given public release, it must be cleared through the site Technical Information Office which will see that the proper patent and technical information reviews are completed in accordance with Energy Systems Policy.

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

FILE - ER DMC - RC
DRP File Room

**The Stability of ClO_2 as a Product
of Gas Phase Decontamination Treatments**

D. W. Simmons

Date Published -- September 1994

Prepared by the
Oak Ridge K-25 Site
Oak Ridge, Tennessee 37831-7101
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

CONTENTS

Summary	v
Introduction	2
Experimental	4
Discussion	5
Conclusions	6
Acknowledgements	7
References	8

Summary

The gas phase decontamination project is investigating the use of chlorine trifluoride (ClF_3) to fluorinate nonvolatile uranium deposits to produce uranium hexafluoride (UF_6) gas. The potential existence of chlorine dioxide (ClO_2) during gas phase decontamination with ClF_3 has been the subject of recent safety discussions.

Some of the laboratory data collected during feasibility studies of the gas phase process has been evaluated for the presence of ClO_2 in the product gas stream. The preliminary evidence to date can be summarized as follows.

- ClO_2 was not detected in the flow loop in the absence of ClF_3 .
- ClO_2 was not detected in the static reactors in the absence of both ClF_3 and ClF .
- ClO_2 was detected in a static reactor in the absence of all fluorinating gases.

The experimental evidence suggests that ClO_2 will not exist in the presence of ClF_3 , ClF , or UF_6 . The data analyzed to date is insufficient to determine the stability of ClO_2 in the presence of ClO_2F . Thermodynamic calculations of the $\text{ClF}_3 + \text{H}_2\text{O}$ system support the experimental evidence, and suggest that ClO_2 will not exist in the presence of ClO_2F .

Additional experimental efforts are needed to provide a better understanding of the gas phase ClF_3 treatments and the product gases. However, preliminary evidence to date suggests that ClO_2 should not be present as a product during the normal operations of the gas phase decontamination project.

Introduction

The gas phase decontamination project is investigating the use of chlorine trifluoride (ClF_3) to fluorinate nonvolatile uranium deposits to produce uranium hexafluoride (UF_6) gas.¹ The long term low temperature *in-situ* process has been identified as a promising candidate for the recovery of uranium holdup in the gaseous diffusion process buildings.²

The laboratory effort to date has evaluated the percent recovery of uranium deposits on typical cascade materials. Quantitative results have been provided by radiological survey before and after the treatment, change in sample weight, chemical analysis, and gas stream concentrations determined over time by infrared spectroscopy. The visual appearance of the sample has been recorded for qualitative analysis.

The uranium deposits have been predominately uranyl fluoride, with reduced fluoride content ranging from less than one percent to as much as twenty percent. The reaction of ClF_3 with uranyl fluoride can be related simply as

with various potential secondary reactions acknowledged, as reported by Shrewsberry and Williamson.³ The existence of the uranyl fluoride in a moist environment, allowing hydration of the deposit, complicates the chemistry additionally. Experiments during the feasibility study with wet uranyl fluoride deposited in copper seal exhaust pipe provided the approximate reaction

which appears plausible if one includes the side reaction of ClF_3 with the deposit's absorbed water, the water of hydration of the deposit, and any residual water in the system. The reaction of ClF_3 and water was determined by Bougon *et al* to be ⁴

initially, but depending on reaction conditions, secondary reactions with the products yielded a variation of products consisting of ClO_2F , ClF , HF , Cl_2 , O_2 , and ClO_3F . The authors noted that ClO_2 cannot exist in the presence of ClF or ClF_3 , since fluorination would yield

and

They also found that the reaction

occurred on warming from -195°C to room temperature, with the ClO_2 susceptible to decomposition as expressed by

Cooper *et al* confirmed the work of Bougon, and confirmed the existence of FCIO as a primary product of the reaction of ClF_3 and H_2O that disproportionates to an equilibrium mixture of mainly ClO_2F and ClF with a half-life of 25 seconds.⁵

Shrewsberry and Williamson also evaluated the potential existence of ClO_2 as a product of the reaction of ClF_3 and uranyl fluoride, as reported by Ellis and Forrest, who had detected small quantities of ClO_2 present at lower reaction temperatures.⁶ Shrewsberry prepared mixtures of ClO_2 with ClF_3 or UF_6 and in each case the ClO_2 was rapidly converted to ClO_2F .

The potential existence of ClO_2 during gas phase decontamination with ClF_3 has been the subject of recent discussion. The experimental evidence of the potential of ClO_2 as a product in the absence of ClF_3 is presented.

Experimental

The experimental systems were described in detail in reference 1. The 4 liter flow loop consisted of a 2 in. id nickel reactor with monel, copper, and stainless steel tube and vacuum components typical to halogen chemistry research. The static reactors were simple 2 liter stainless steel vessels. The preliminary analysis of the IR spectra collected revealed that:

1. ClO_2 was not detected in the flow loop in the absence of ClF_3 during gas-phase treatments.

Gases detected by infrared spectroscopy were UF_6 , ClF , ClO_2F , HF , and occasional trace quantities of ClO_3F and what is believed to be FCIO . The flow loop was not allowed to remain for extended periods without ClF_3 , so the appearance of ClO_2 in the absence of any of the other fluorinating agents was not investigated.

The gases were analyzed on-line only by infrared spectroscopy, using a 6 cm. monel gas cell with AgCl windows in a Nicolet FTIR. The presence of F_2 , Cl_2 , O_2 , N_2 , or any other infrared non-absorber can therefore not be confirmed or disputed experimentally.

2. ClO_2 was not detected in the long term static reactors in the absence of ClF_3 and ClF .

Following consumption of the ClF_3 , the ClF was observed slowly decreasing, with a resultant increase in UF_6 . Gas samples have been acquired with both the ClF_3 and the ClF consumed. IR detectable gases in the product were UF_6 , ClO_2F , HF , and trace ClO_3F and FCIO on occasion.

3. ClO_2 was detected in the long term static reactor in the absence of all fluorinating gases.

In an experiment conducted in the presence of NaF pellets, following the consumption of ClF_3 and ClF , the consumption (or dissociation) of ClO_2F , and the trapping of the UF_6 and most of the HF by the NaF , an IR spectrum showed small quantities of ClO_2 , ClO_3F , HF , and CO_2 . A gas sample was made available for mass spectroscopy evaluation in another lab, however anomalies with this new system provided little quantitative data. Both oxygen and chlorine species were dominant in the analysis.

The static reactors did not have an on-line FTIR. The few gas samples were acquired during the brief downtime of the flow loop experiments. The gas cell was inserted in the system exhaust preceding the chemical trap, the gases expanded and allowed to equilibrate in the additional (minor) volume. There was not a method to "mix" the gases prior to sampling. The presence of moist air as a result of the sampling was monitored by acquiring several spectra over a short time and comparing to the initial spectrum. An increase in HF , CO_2 , and H_2O was indicative of additional air being ingested. If a major presence of air was suspected, the sample was redrawn.

Discussion

The detection of minor quantities of ClO_2 in the presence of ClO_2F by infrared spectroscopy is not trivial. The strongest band of ClO_2 , the ν_3 fundamental is a *P-Q-R* centered at 1105 cm^{-1} ($9.05\text{ }\mu$), which is also the center of the *P-Q-R* ν_1 fundamental of ClO_2F . The concentration of ClO_2F is expected to be much greater than ClO_2 , preventing the obvious detection of the ClO_2 band. Smith *et al* reported in GAT-T-687 that an intensity ratio of the 1273 cm^{-1} band to the 1105 cm^{-1} band of ClO_2F of less than 100:43 was indicative of the presence of ClO_2 in ClO_2F .⁷ However, Arvia and Aymonino mentioned that chlorine dioxide formation in the presence of ClO_2F was dubious, even in the absence of fluorine.⁸ Their published spectrum of ClO_2F gave the ratio of the two bands as 100:40.

The spectra evaluated during the gas-phase treatments has had a ratio of 100:40 - 45 for the $1273:1105\text{ cm}^{-1}$ bands of ClO_2F , with the exception of the third example. ClO_2 has not been detected at the ν_1 fundamental at 945 cm^{-1} . This peak is much weaker than the band at 1105 cm^{-1} , and would require a much larger concentration of ClO_2 present for detection.

Unfortunately, calibration spectra of ClO_2F and ClO_2 were not available. The spectrum of ClO_2F has been well characterized in the past, allowing calculation of the absorbance constants. The absorbance constants for ClO_2 , however, are not available in this laboratory. By employing only infrared spectroscopy, particularly without calibration spectra of the suspected constituents, it is possible that small quantities of ClO_2 could be present but not detected experimentally.

Preparation of ClO_2 and ClO_2F in the laboratory would allow calibration spectra to be obtained of these compounds. The calibration spectra could then be used to spectrally subtract the other species from the spectra already collected, allowing a more detailed analysis of the presence of ClO_2 in the product. The availability of pure samples would also provide the capability for evaluation of the stability and reactivity of ClO_2 and ClO_2F as treatment gas products.

Ideally, a mass spectrometer or corrosive gas chromatograph should be employed on-line in future experiments to also allow detection of the diatomic species, such as F_2 , Cl_2 , O_2 , etc.. The presence (or absence) of these gases could effect the stability of the product gases, or instigate additional concerns (ie, the presence of AlCl_3 , more severe corrosion problems, disposal of Cl_2). A clearer understanding of the product gases is needed to better predict the treatment success and residual gas stream resulting from gas phase ClF_3 treatments in the cascade.

Conclusions

The primary objective of the gas-phase work to date has been the demonstration of the removal of uranium compounds from gaseous diffusion substrates. All spectra collected have not been analyzed specifically for the presence of ClO_2 or other minor gas phase constituents. However, the data that has been analyzed indicate that ClO_2 will not exist in the presence of fluorinating agents such as ClF_3 , ClF , or UF_6 . Assuming the presence of at least one of these three species at all times, ClO_2 is not anticipated as a gas phase species during the normal operations of the gas phase decontamination project.

Thermodynamic calculations by Trowbridge of the $\text{ClF}_3 + \text{H}_2\text{O}$ system support the experimental evidence gathered to date, showing what species should be stable in the presence of ClO_2 .⁹ The calculations also suggest that ClO_2 would not exist in the presence of ClO_2F . Experimental evidence on the stability of ClO_2 in the presence of only ClO_2F has not been examined at this time.

A more comprehensive analysis of the data collected during the demonstration of the process feasibility should be conducted. The analysis could provide more definitive results or illuminate areas still needing experimental work. This would allow us to better predict not only the results of gas phase decontamination with ClF_3 , but also the safety of handling the product gases. If a decision is made to recycle the product gases of the ClF_3 gas phase decontamination process, the need for additional knowledge of the chemistry of the chlorine - oxygen - fluorine systems will become even more important.

Acknowledgments

The author would like to thank Dr. L. D. Trowbridge for his frequent discussions and many helpful comments regarding the chemistry of the chlorine fluorides, oxides, and oxyfluorides. The author also would like to thank Drs. D. P. Armstrong, R. D. Bundy, and L. D. Trowbridge for their prompt review and critique of this document.

References

1. E.B. Munday and D.W. Simmons, *Feasibility of Gas-Phase Decontamination of Gaseous Diffusion Equipment*, K/TCD-1048, Martin Marietta Energy Systems, Oak Ridge K-25 Site, February 1993.
2. E.B. Munday, *Preconceptual Design of the Gas-Phase Decontamination Demonstration Cart*, K/TCD-1076, Martin Marietta Energy Systems, Oak Ridge K-25 Site, December 1993.
3. R.C. Shrewsberry and E.L. Williamson, "Chemistry of the Chlorine Trifluoride - Uranyl Fluoride Reaction", J. Inorg. Nucl. Chem. **28**, 2535 - 39, (1966).
4. R. Bougon, M. Carles, and J. Aubert, "The Reaction of Chlorine Trifluoride with Water", C.R. Acad. Sc. Paris **265**, 179 (1967).
5. T.D. Cooper, F.N. Dost, and C.H. Wang, "Evidence for ClOF as a Primary Product of the Reaction of ClF₃ with H₂O", J. Inorg. Nucl. Chem. **34**, 3564 - 67, (1972).
6. J.F. Ellis and C.W. Forrest, "Some Studies in the Inorganic Chemistry of the Reaction Between Uranyl Fluoride and Chlorine Trifluoride", J. Inorg. Nucl. Chem. **16**, 150 -153, (1960)
7. E.A. Smith, F.C. Steinbach, and K.E. Beu, "Infrared Spectra of ClO₂, ClO₂F, and ClO₃F", GAT-T-687, Goodyear Atomic Corp., December 1959.
8. A.J. Arvia and P.J. Aymonino, "Infra-red Absorption Spectrum of Gaseous Chloryl Fluoride (FClO₂), Spec. Acta **19**, 1449 - 56, (1963).
9. L.D. Trowbridge, "ClF₃ + H₂O Thermodynamics and Kinetics", letter to R.T. Shelton, July 1993.

Distribution

Martin Marietta Energy Systems, Inc. Oak Ridge

M. H. Albert
W. D. Altman
D. P. Armstrong
W. D. Bostick
D. H. Bunch
R. L. Fellows
M. J. Haire
J. R. Hale
L. C. Hensley
D. P. Hoffman
R. K. Kibbe
L. D. Ladd
A. F. Love
E. B. Munday
D. W. Neiswander
D. W. Simmons (3)
L. D. Trowbridge

Martin Marietta Utility Services, Inc. Oak Ridge

E. J. Barber
R. L. Ritter

Portsmouth

R. J. Riddle
A. J. Saraceno
C. A. Welch