



**ENVIRONMENTAL  
RESTORATION  
PROGRAM**

**Technical Bases for the Use of  $\text{ClF}_3$   
in the MSRE Reactive Gas Removal Project  
at Oak Ridge National Laboratory,  
Oak Ridge, Tennessee**

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Oak Ridge, Tennessee**

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Technical Bases for the Use of  $\text{ClF}_3$   
in the MSRE Reactive Gas Removal Project

Molten Salt Reactor Experiment Project

ENVIRONMENTAL RESTORATION PROGRAM

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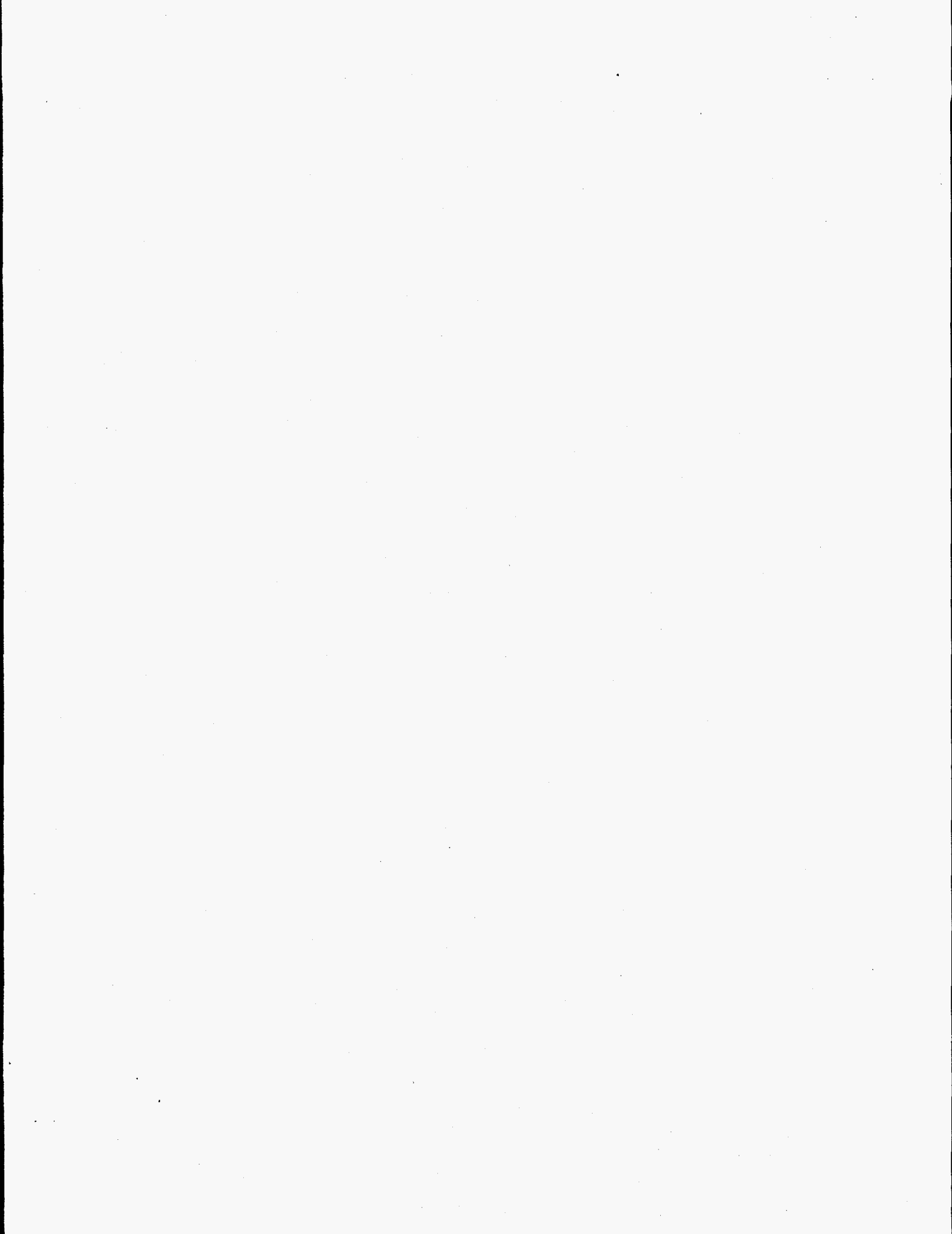
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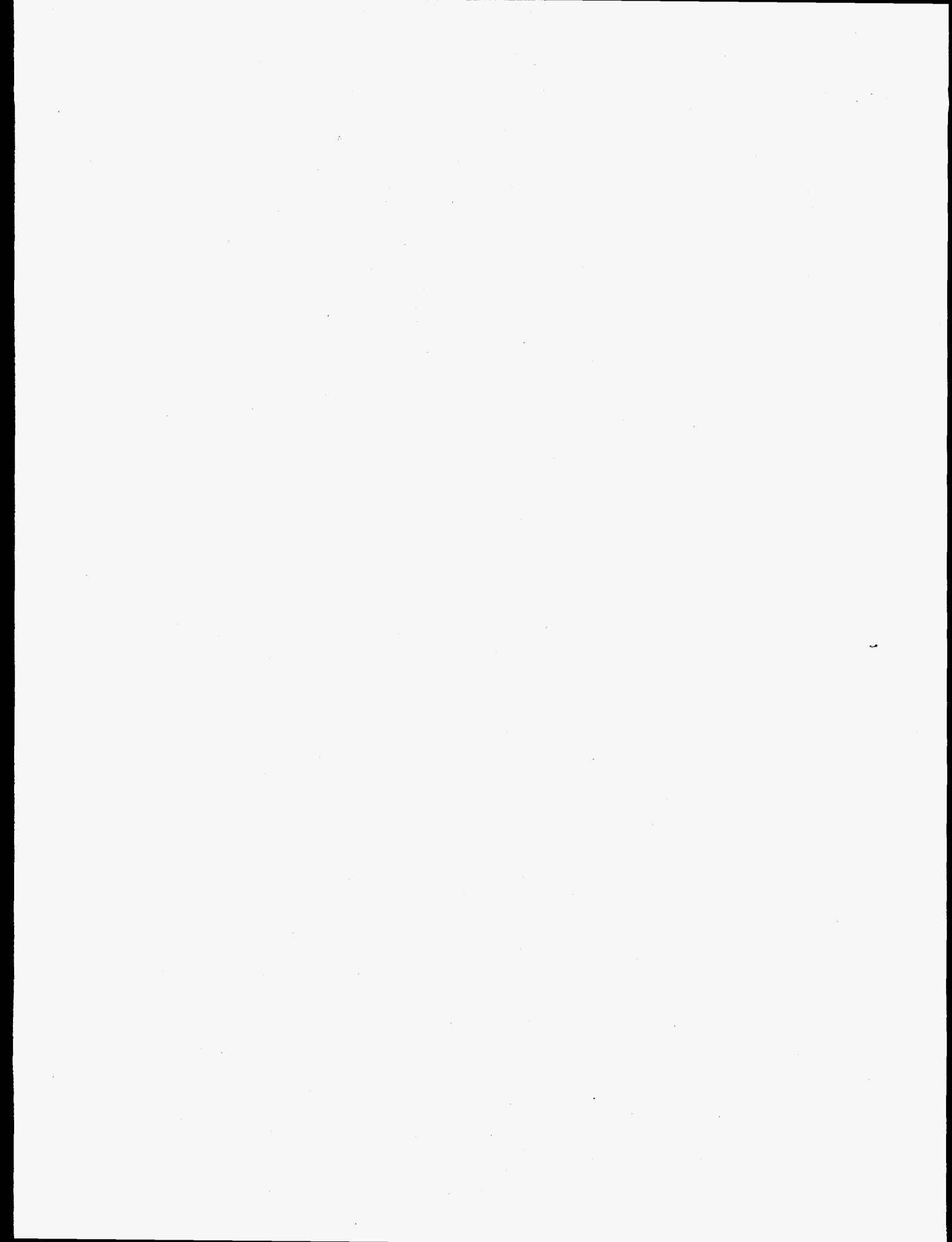
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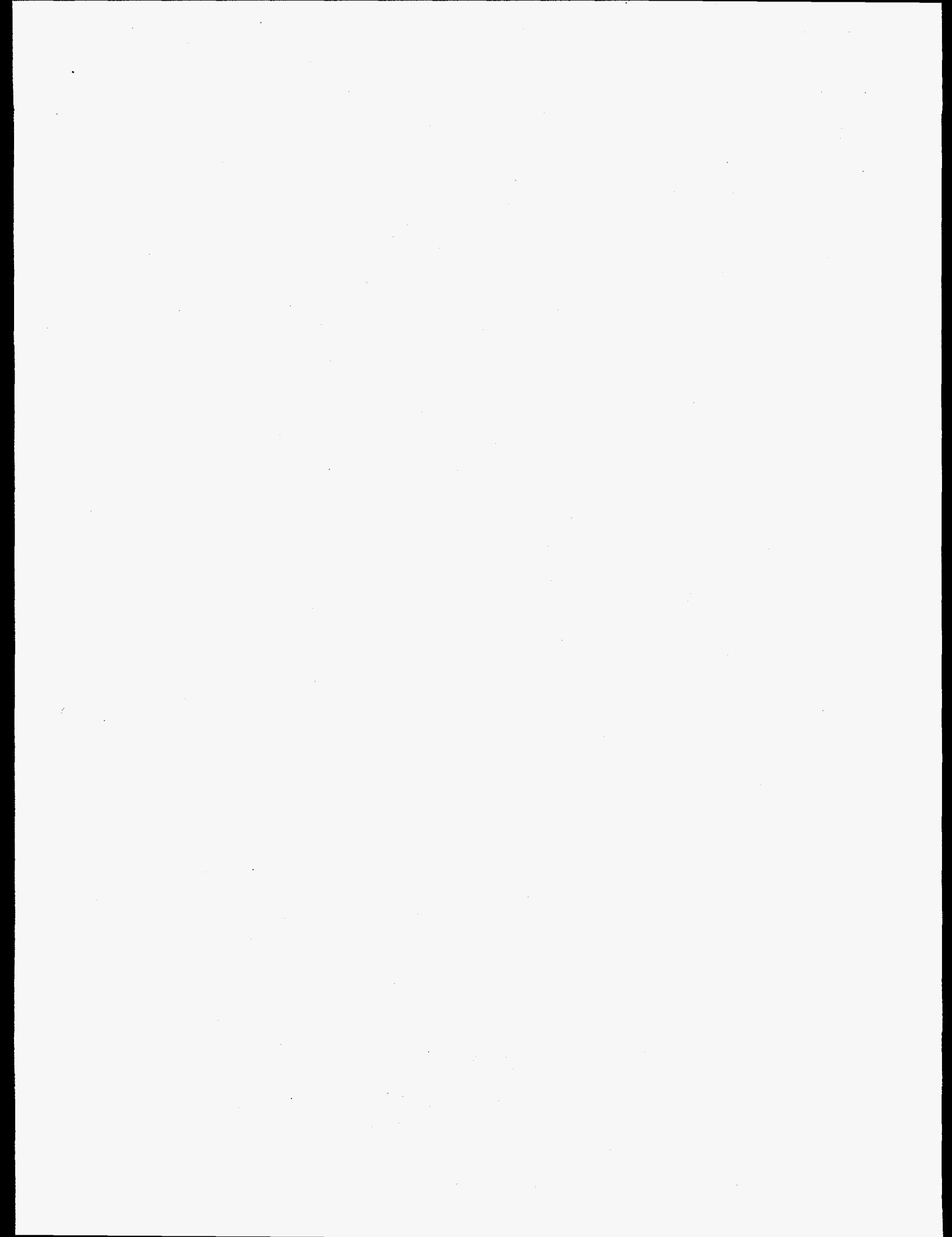




## PREFACE

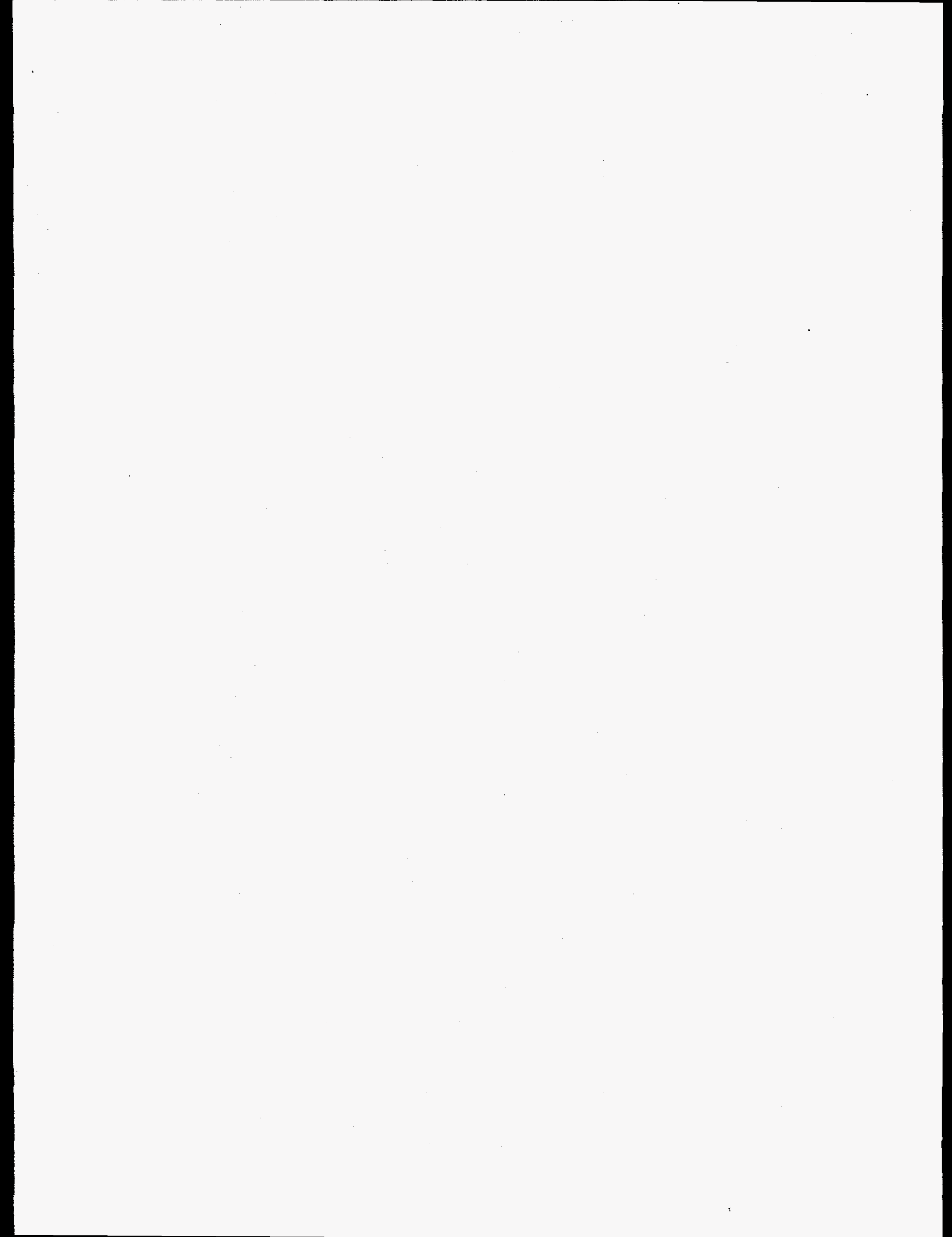
This report discusses the technical bases for the use of  $\text{ClF}_3$  treatments to chemically convert non-volatile deposits in the Molten Salt Reactor Experiment (MSRE) off-gas piping to  $\text{UF}_6$ , which can then be removed as a gas. This process is important to remediation of MSRE because the deposits, which are nearly impermeable, are impeding the removal of reactive gases from that system. A variety of issues are examined, including the efficacy of  $\text{ClF}_3$  at deposit removal under the conditions imposed by the MSRE system, materials compatibility of  $\text{ClF}_3$  and its reaction products, and operational differences in the Reactive Gas Removal System imposed by the presence of  $\text{ClF}_3$  and its products.

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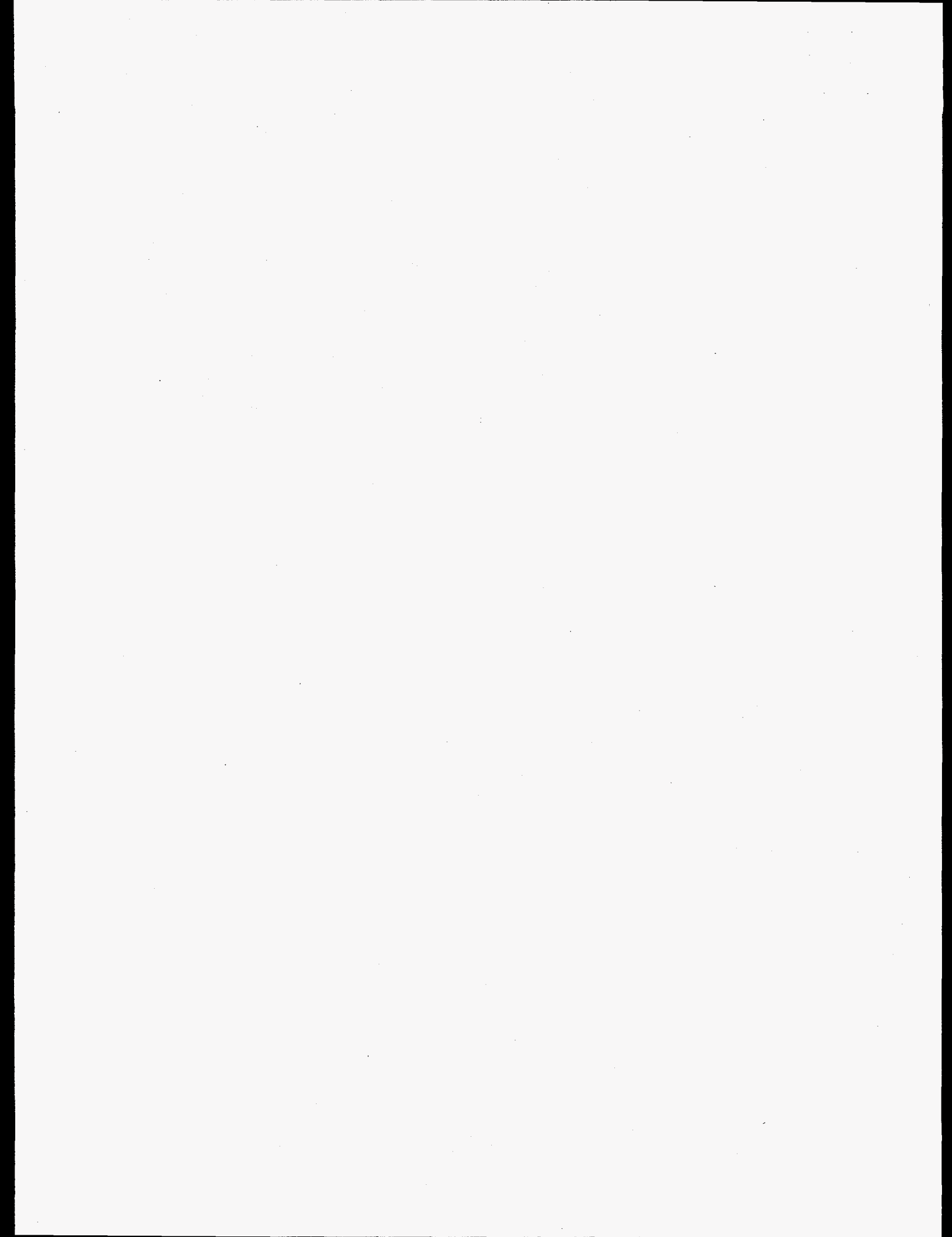
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## ABBREVIATIONS

ACB	activated carbon bed
IR	infrared
MSRE	Molten Salt Reactor Experiment
PTFE	polytetrafluoroethylene
RGR	Reactive Gas Removal
RGRS	Reactive Gas Removal System



## EXECUTIVE SUMMARY

Nearly impermeable, non-volatile deposits in the Molten Salt Reactor Experiment (MSRE) off-gas piping are impeding the removal of reactive gases from that system. The deposits almost certainly consist of reduced uranium fluorides or of uranium oxyfluorides. Treatment with  $\text{ClF}_3$  is a non-intrusive method capable of chemically converting these compounds back to  $\text{UF}_6$ , which can then be removed as a gas. This report discusses the technical bases for the use of  $\text{ClF}_3$  treatments in this system. A variety of issues are examined, and where the necessary information exists or has been developed, the resolution discussed. The more important of these issues include the efficacy of  $\text{ClF}_3$  at deposit removal under the conditions imposed by the MSRE system, materials compatibility of  $\text{ClF}_3$  and its reaction products, and operational differences in the Reactive Gas Removal System imposed by the presence of  $\text{ClF}_3$  and its products.

# 1. INTRODUCTION

The discovery that uranium (of the highly radioactive 233 and 232 isotopes) had migrated from the fuel salt in the Molten Salt Reactor Experiment (MSRE) was considered sufficiently serious to warrant the present extensive program for remediation.  $F_2$  gas containing  $UF_6$  at or near saturation levels had built up to near atmospheric pressure, and some of the uranium was found to be migrating and accumulating in the entrance zone of the activated carbon bed (ACB). The situation as a whole had the attention of not only the contractor management and DOE, but also external oversight (e.g., Defense Nuclear Facilities Safety Board) and the public news media. The remediation program was intended to limit the growth of hazardous conditions, then systematically address and remove those conditions. An initial effort, already completed, is to prevent further buildup of uranium in the ACBs and to minimize the potential consequences of an exothermic reaction of trapped fluorine and uranium in the carbon (a low probability, but potentially serious event). The measures taken to alleviate that concern isolate the carbon beds from the remainder of the off-gas system and MSRE fuel drain tanks, leaving no exit for the slowly increasing pressure of radiolytically produced  $F_2$ . The second stage of the remediation effort, then is to provide a means of safe removal of these gases. This phase is termed the Reactive Gas Removal (RGR) project.

The intent of the RGR portion of the MSRE remediation effort is to remove the gases, in particular the reactive components  $F_2$  and  $UF_6$ , from the off-gas system. The  $F_2$  evolved from the MSRE fuel salt by radiolysis, and the  $UF_6$  was generated similarly by an as yet incompletely understood chemical and radiolytic process. The technical bases of the methods chosen for removing and processing the reactive gases were discussed in an earlier report (*Trowbridge 95a*). The intent of this report is to supplement that report, covering the technical bases for use of  $ClF_3$  for the purpose of volatilizing uranium-containing deposits which are impeding gas flow in that system.

The partial pressure of  $UF_6$  in the MSRE off-gas piping has been measured to be near the saturation vapor pressure for solid  $UF_6$ , so it is plausible that solid deposits of  $UF_6$  exist in cooler sections of the line. Early in the planning of the RGR project, it was recognized that such solid deposits could plug the line, temporarily impeding communication of the RGR System (RGRS) with the full volume of the MSRE. Eventually, however, as the pressure is lowered, solid  $UF_6$  deposits will sublime and can be removed by pumping or inert gas purging.

Since the beginning of the actual gas removal operation, it has become obvious that the MSRE piping system is blocked in several places by non-volatile plugs. Since the first two plugs encountered did not sublime when the RGR pressure was lowered far below the vapor pressure of  $UF_6$ , and absent any other plausible mechanism for the formation of solid plugs, it is concluded that the plugs consist of  $UO_2F_2$  (or related compounds, such as  $UOF_4$ ) created by hydrolysis of  $UF_6$  by inleaking moisture,  $UF_5$  (or related compounds such as  $UF_3$  or  $UF_4$ ) formed by the radiolysis of solid  $UF_6$ , or  $UF_6$  with a coating of either of the above classes of non-volatile species.

It is obviously desirable to non-intrusively eliminate such plugs, at least to the extent of reestablishing gas flow between all sections of the MSRE piping that may have  $F_2$  and  $UF_6$  in them. The alternative for gas recovery is to construct additional access points in the piping and fuel tanks. While beyond the scope of the RGR project, removal of all uranium from the MSRE is a program goal. For this reason it is desirable to have a method capable of converting any uranium deposit, whether it physically obstructs a line or not, to  $UF_6$ , allowing its removal.



Workable options for removal of uranium plugs are limited. Physical removal (e.g., pipe disassembly) in light of the highly radioactive nature of the uranium isotope mix would be extremely inconvenient, to say the least. Liquid solution methods also are likely to be deemed unsafe and impractical for many reasons, including the difficulty of introducing and removing liquids, solution mixing difficulties within MSRE, nuclear criticality for hydrogen-containing solvent systems (e.g., water or anhydrous HF), and materials compatibility, to name a few. The only method that seems to offer hope of remote removal of solid deposits is the chemical conversion of the plug back to  $UF_6$  by means of reactive gases.

In principle,  $F_2$  can react with any plausible plug materials to produce  $UF_6$ . Rates of reaction of  $F_2$  with  $UF_4$ ,  $UF_5$  and  $UO_2F_2$  are known, however, and are too low at MSRE ambient temperatures to be useful. Simply from a logical standpoint, if plugs have indeed formed,  $F_2$  must not be effective at reconversion to  $UF_6$  at ambient temperature, since  $F_2$  is currently present at fairly high partial pressure. For  $F_2$  to be effective at recovery of  $UF_4$  or  $UF_5$  plugs, somewhat elevated temperatures would be necessary, on the order of 250 to 300°C; for effectiveness at recovery of  $UO_2F_2$  plugs, temperatures at least 100 degrees higher would be needed.

An alternative fluorinating agent that has often been used for deposit removal is  $ClF_3$ . Reaction rates of  $ClF_3$  with  $UF_4$ ,  $UF_5$  and  $UO_2F_2$  are likewise reasonably well known and are considerably faster than those of  $F_2$ . There are additional materials and waste handling problems that will have to be addressed if  $ClF_3$  is used, but by and large, systems that can handle  $UF_6$  and  $F_2$  can also handle  $ClF_3$  successfully.

Other interhalogen fluorinating agents could also be considered (e.g.,  $BrF_3$  or  $IF_7$ ), but their behavior is not nearly so well characterized as  $ClF_3$ , and both create much more complicated materials compatibility problems than  $ClF_3$ , which outweigh any potential benefits of possible higher reaction rates. More active agents known to be effective (and plausibly providing more rapid reaction than  $ClF_3$ ) are also known (e.g., atomic fluorine,  $F_2O_2$ , and  $KrF_2$ ) but are thermodynamically and kinetically unstable at MSRE conditions. They would therefore require on-site and probably in situ generation, and would be much more complicated to implement in MSRE than the addition of a reactive, but stable gas such as  $ClF_3$ .

Another point in favor of  $ClF_3$  over other compounds is the relative familiarity with its use on the part of many members of the MSRE team. Utilizing a less familiar material or process would almost surely require more time in development, familiarization and qualification. Still, there are other materials that could be used, some of which would probably prove technically viable.

An approximate sequence for the use of  $ClF_3$  for removal of a line plug in the MSRE might be:

1. Prepare a treatment gas mix of consisting of  $ClF_3$ , an inert diluent, and a small fraction of  $F_2$  (the reasons for the last two components will be explained below).
2. Evacuate the (accessible) MSRE pipe section containing the plug.
3. Introduce the treatment gas mix into the MSRE pipe section.
4. Allow reaction to proceed for a prescribed period of time
5. Pump out gas, monitoring its composition to determine the character of the deposits, quantity of  $UF_6$  recovered and of  $ClF_3$  consumed.  $UF_6$  will be adsorbed in the existing NaF trap; the remainder of the reaction gas may be disposed of (via traps) or reused, depending on the degree of  $ClF_3$  consumption and the details of the treatment method.

6. Repeat 3-5 until the deposit has been successfully removed (the definition of success being a strategy decision, discussed later).

There are several major (and numerous minor) issues which need to be recognized and addressed if  $\text{ClF}_3$  is used for deposit removal in the MSRE. Some of these are:

1. Efficacy of  $\text{ClF}_3$  Treatment: The nominal rates of reaction are not particularly high at MSRE temperatures. More seriously, practical reaction rates may be further limited by diffusion of gaseous reactants and products, which can be a very slow process in long piping runs. Some form of gas mixing enhancement may be needed to make plug recovery in a reasonable period of time a practical matter. This problem will be obviated somewhat if working on a slightly permeable plug under circumstances in which  $\text{ClF}_3$ -containing treatment gas can be forced through the plug.
2. Gas handling -- Methods of handling and mixing  $\text{ClF}_3$  and its reaction products will vary somewhat from those used for the  $\text{F}_2/\text{HF}/\text{UF}_6$  gas mix encountered so far.
3. Gas disposal -- Unlike  $\text{F}_2$ ,  $\text{ClF}_3$  and its reactive reaction products will not be totally consumed and converted to innocuous gases in the current trapping system.  $\text{Cl}_2$  and chlorine oxides may be produced from reaction of  $\text{ClF}_3$  (or of its reaction products) with the activated alumina or molecular sieve traps. Either the off-gases will have to be vented (per permit) or additional gas scrubbing systems installed.
4. Materials compatibility -- Most materials compatible with  $\text{F}_2$  and  $\text{UF}_6$  will be compatible with  $\text{ClF}_3$ . IR optics may be more prone to degradation. Materials compatibility questions include not only the effects of  $\text{ClF}_3$ , but also pre- and post-trap reaction products, especially  $\text{Cl}_2$ , which may have a detrimental effect on metals, especially aluminum components.

These issues, as well as various other minor ones, will be described in the next section in more detail. Where information is available, or has been developed in the course of preparation for use of  $\text{ClF}_3$ , the resolution of these issues will be covered as well.

## 2. DISCUSSION OF ISSUES

A considerable number of issues will have to be considered and addressed in order to permit use of  $\text{ClF}_3$  to assist in removal of reduced or hydrolyzed uranium-containing deposits in the MSRE off-gas system. In this section, we itemize in more detail major and minor issues. While the general intent of this document is not necessarily to address and lay to rest every issue, where an obvious or plausible resolution exists, it will be discussed.

In the introduction, four main issue areas were listed: (1) efficacy of  $\text{ClF}_3$  Treatment; (2) gas handling; (3) gas disposal; (4) materials compatibility. The categories, of course, are artificial, generated for purposes of organizing the discussion. Within each area, the discussion is further subdivided into a variety of sub-issues. Many of the issues and sub-issues are interrelated. For example, material compatibility is a potential issue within the areas of gas handling and gas disposal.

### 2.1 EFFICACY OF $\text{ClF}_3$ TREATMENT

One obvious issue relating to the use of  $\text{ClF}_3$  in the MSRE is its ability to do the intended job. A variety of factors influence this. On a strategic level, the efficacy of treatment will depend a good deal on exactly what the intended goal of the treatment program is to be. Beyond this are a variety of physical and chemical factors that will influence the effectiveness and speed of conversion of solid uranium compounds to  $\text{UF}_6$ , among which are the physical and chemical nature of the deposit, the chemical reaction rate of  $\text{ClF}_3$  with various uranium compounds, mass transport limitations of reaction rate, and logistic factors affecting the economics of the process.

Program Goal — Defining "success": To some extent, the optimum method chosen may be dictated by the goal of a cleanup treatment program. Several potential goals come to mind. A suitable treatment scheme for one may not be suitable for all. Three possible goals of  $\text{ClF}_3$  treatment are:

1. Consume and remove deposits plugging pipes sufficiently to allow gas flow communication with all sections of the MSRE piping.
2. Consume and remove all reduced or hydrolyzed uranium fluoride deposits outside of the fuel salt drain and flush tanks.
3. Consume and remove all uranium from the fuel salt.

The discussions in this report mainly relate to the first of these and are generally applicable to the second. The third possible goal is not discussed in this report.

Deposit Character: - The nature and location of solid deposits will have a significant effect on the ability to convert them to gaseous  $\text{UF}_6$ , which is obviously the most convenient chemical form for removal of uranium from the MSRE system. Three general possibilities exist for the chemical form. These are (1) solid  $\text{UF}_6$  coated with nonvolatile uranium compounds, (2) reduced uranium fluoride ( $\text{UF}_5$ ,  $\text{UF}_4$ ,  $\text{UF}_3$ ,  $\text{U}_2\text{F}_9$ , or  $\text{U}_4\text{F}_{17}$ ), or uranium oxyfluorides ( $\text{UO}_2\text{F}_2$ , its hydrates,  $\text{UOF}_4$ , or any of several other related forms).

It is very plausible, almost inevitable, that solid  $\text{UF}_6$  deposits formed in the MSRE off-gas piping system at some point. The few measurements of partial pressure of  $\text{UF}_6$  gas have yielded values that correspond to its saturation vapor pressure at a temperature only slightly below ambient,

and thus imply the existence of solid  $UF_6$  deposits in locally cool spots (e.g., locations that are in better than average thermal contact with the ground, which, in East Tennessee, has an average temperature of approximately  $14^\circ C$ ). Such a deposit should present no more than a temporary problem, in that it should sublime at a rate dictated by the slower of the rate of gas removal from the vicinity of the plug (via pumping or diffusion) or heat transport to the subliming surface of the deposit.

Reduced uranium fluorides ( $UF_3$ ,  $UF_4$ ,  $UF_5$ , or related intermediate fluorides) may form from radiolysis or possibly by oxidation-reduction reactions (e.g., corrosion of metals of construction by  $UF_6$  or by reaction of  $UF_6$  with carbon or hydrocarbons).

Solid highly enriched uranium (highly enriched  $UF_6$ , enriched, that is, in U-235 and U-234) has been known to generate reduced uranium fluorides by radiolysis (i.e.,  $UF_6$  can be dissociated by its own  $\alpha$  radiation, forming  $UF_5$  and  $F_2$  (*Saraceno 88*)). The MSRE isotopic mix is much more radioactive than highly enriched uranium, so should generate reduced uranium more rapidly than highly enriched  $UF_6$ . Gaseous  $UF_6$  can similarly be reduced by radiolysis (*Rosen 51; Wendolkowski 54*), but in the presence of additional gaseous  $F_2$ , the immediate radiolysis product ( $UF_5$  gaseous monomer) is apparently reconverted to  $UF_6$  before it has the opportunity to agglomerate to the more fluorination-resistant bulk solid (*Becker 82; Lyman 87*). On the other hand, the presence of a large partial pressure of  $F_2$ , already known to have somehow converted  $UF_4$  in the fuel salt to  $UF_6$ , suggests that the radiolysis might be reversed, at least at the surface of a deposit. This reversal, if it occurs, might be due to the action of radiolytically produced atomic fluorine. Recent experimental attempts to duplicate  $UF_6$  generation from irradiated fuel salt have been successful only at elevated temperatures (i.e. during simulated salt annealing) (*Toth 97*). Thus it is not known whether a means exists of reversing radiolysis in deposits remote from the fuel salt at room temperature.

Reaction of  $UF_6$  with water (e.g., from air leakage or water permeation of elastomer gaskets or seals) will result in formation of  $UO_2F_2$ . Excess water will result in formation of a hydrate of  $UO_2F_2$ ; excess  $UF_6$  may result in the formation of an oxyfluoride with more F and less O, e.g.,  $UOF_4$  or  $U_2O_3F_6$ . Since water and HF can slowly dissolve in and diffuse through such materials, deposits in contact with humid air on one side and  $UF_6$  on the other may have a layered structure with higher hydrates on the air side and fluorine rich oxyfluorides on the  $UF_6$  side.

Deposits formed by radiolysis of solid  $UF_6$  should be expected anywhere solid  $UF_6$  could form permanently. Since the  $UF_6$  originates primarily in the fuel salt drain tanks and is consumed in the ACB, its concentration should be highest at the source (the drain tanks) and lowest at the sink (the ACB).  $UF_6$  solid deposits can be expected anywhere that the wall temperature drops low enough to desublime  $UF_6$ . The first likely location for this is the exit of the drain tanks (warmed as they are by radiation heating), and indeed plugs seem to have formed in that general vicinity. Later plugs should occur wherever a locally colder spot exists, in a region in better thermal contact with the earth. Other plugs (in fact the first ones encountered in RGR operation) seem to be at wall penetrations. Temporary deposits could form in areas in relatively good thermal contact with the ambient air, forming when cold weather and nighttime temperatures cool the pipe below the saturation temperature of  $UF_6$ . Such deposits should sublime, however, when the temperature rises.

Stubborn deposits of solid uranium compounds in the uranium enrichment industry most commonly are of the oxyfluoride variety rather than reduced fluorides. In MSRE, deposits formed by reaction of  $UF_6$  (solid or gaseous) with inleaking moisture should occur at the site of the leak (unless the inleaking airflow were to overwhelm the  $F_2/UF_6/He$  flow from drain tanks to ACB, in which case it should form in the region of mixing of the two gas flows). An episodic inleakage of

large amounts of air could convert a layer on the surface of a solid  $UF_6$  deposit to  $UO_2F_2$ . If such a layer were sufficiently thick, it might make the deposit appear to be non-volatile.

Most of the evidence to date tends to support the solid  $UF_6$ -radiolysis mechanism. A plausible scenario for deposit formation is as follows:

1.  $UF_6$ , formed in the fuel salt region, diffuses or convects to more remote areas of the off gas piping.
2. At some point, the  $UF_6$ , near its vapor pressure in warmer sections of the piping, encounters a locally cooler region of piping and desublimates, forming a solid deposit and eventually a plug.
3. Radiolysis of  $UF_6$  occurs in the gas phase and solid phase, but is reversed in the gas phase, and possibly on the surface of the solid, but is more permanent in the bulk of the solid deposit. A non-volatile reduced uranium compound is formed from the original  $UF_6$  solid deposit.

The importance of the character of the deposit is in their ease of removal or conversion to  $UF_6$ . At room temperature, reduced fluorides can be expected to be essentially unreactive with  $F_2$  but to react measurably with  $ClF_3$ . Oxyfluorides are considered completely unreactive to  $F_2$  at ambient temperature. They have a measurable reaction rate with  $ClF_3$ , though that rate is considerably slower than the corresponding rate of reaction of  $ClF_3$  with reduced fluorides. There is considerable anecdotal evidence to the effect that the different oxyfluoride forms have significantly different reaction rates.

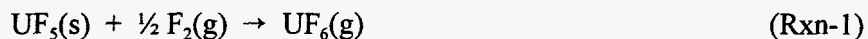
There is not much that can be done about the nature of MSRE uranium deposits, but the best treatment method should be capable of handling all types with some effectiveness. If  $ClF_3$  is used to attack deposits, the nature of the deposits will be revealed by the pattern of  $ClF_3$  reaction products that are pumped out of the system after treatment.

A second factor relating to the nature of the deposits may prove important, and that is the physical distribution of solid. A diffuse layer spread out over large areas of pipe should not impede gas flow, and should be fairly amenable to removal by pumping reactive gas through the affected pipe sections. More localized deposits will present lower surface area to the reactive gas so that the rate of deposit removal may well be limited by the rate of mass transport of  $ClF_3$  to the surface (and reaction products away) rather than by chemical reaction rate per se. The extreme case of this would be when a deposit completely plugs a pipe. In this case, the reactive gas mix will have to be introduced batchwise, and mass transport of  $ClF_3$  down the length of the pipe to the surface of the deposit may be very slow. For most of the deposits discovered to date in MSRE, the plugs seem to be slightly permeable, allowing pressure equalization over the course of several hours or days. Thus, it should be possible to slowly force  $ClF_3$ -containing treatment gas through the plug. Chemical reaction should erode passages through the plug, making it more and more permeable as the treatment continues.

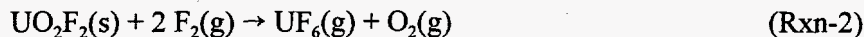
Reaction Rates: The rate of conversion of a deposit will be partly determined by the rate of the chemical reaction with the treatment gas.

There have been many studies of the reactions of uranium fluorides, oxides, and oxyfluorides with  $F_2$ ,  $ClF_3$ , and other fluorinating agents, but few produced quantitative rate data. The rate of reaction of reduced uranium fluorides to produce  $UF_6$  by reaction with  $F_2$  has been measured at somewhat elevated temperatures (*LaBaton 59a*). Measurements at ambient temperatures are sparse or gave no observable rate. The reactions of fluorides lower than  $UF_5$  typically display an induction

period, which is interpreted as conversion of the surface of the fluoride to  $UF_5$ , followed by reaction of  $UF_5$  to form the volatile  $UF_6$  per:

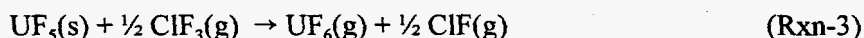


The reaction of  $F_2$  with  $UO_2F_2$  occurs via the following overall equation:



The rate is so slow as to be considered zero at room temperature. Most of the useful quantitative rate information at higher temperatures comes from studies of the fluorination of uranium oxides, (*Iwasaki 64; Yahata 64; Iwasaki 68*) which proceeds via initial conversion of a surface layer to  $UO_2F_2$ .

Similar rates of reaction of uranium deposits with  $ClF_3$  are considerably higher. As with  $F_2$ , fluorination of lower fluorides is presumed (on experimental evidence) to proceed first by conversion of the surface to  $UF_5$  and then to react via:



The corresponding reaction of  $ClF_3$  with  $UO_2F_2$  is frequently given as:



The 1:1 ratio of  $ClO_2F$  to  $ClF$  shown in the product mix is only approximate, as  $ClO_2F$  may diminish in the product mix in favor of corresponding quantities of  $ClF$  and  $O_2$ . Also, in either of the last two reactions,  $ClF$  and  $ClO_2F$  can further react (*Luce 67a; Luce 68; Benoit 70*) producing ultimately  $Cl_2$  and  $O_2$  as final reaction products.  $ClO_2$  was either not observed or only tentatively identified as a trace product during the secondary reaction of  $ClO_2F$  with  $UO_2F_2$  (*Ellis 60; Shrewsberry 66; Luce 67a*).

Though these fluorination reactions have been studied many times, rates are reported in only a relatively few studies. Further, a good deal of the rate information is presented in a manner that renders it difficult to apply with confidence outside the narrow conditions of the particular study. Many factors can influence the rate of a gas-solid reaction, such as surface area, surface morphology, history of the solid, particle size, and macroscopic and microscopic details of gas transport and adsorption, to name a few parameters other than the obvious ones of gas concentration and temperature. All relevant factors may not have been explored in a particular study. This leads to uncertainty when applying reaction rates outside the specific conditions of that study, and frequently leads to seemingly contradictory results when comparing rates reported in different papers. Many rate equations use a form termed the "shrinking sphere" model, but others took into account different factors and use different equation forms.

It would be useful to definitively rationalize the mass of rate data for the uranium fluorides and oxyfluorides, but that effort is beyond the scope of this work. Nevertheless, for purposes of comparison this report attempts to convert reported rates to a common unit basis, listing rate constants in units of reciprocal time. Though it is an oversimplification to do so, it may be convenient to think of this rate as the characteristic lifetime for the particles being reacted. Unfortunately, the sizes and other properties of the test materials varied considerably from one report

to another, so the rates aren't truly directly and quantitatively comparable. They can, however, provide an order-of-magnitude guide to relative reaction rates.

Fluorine rates are reported only at fairly elevated temperature. Extrapolation of temperature dependent data to room temperature is not likely to be accurate.  $\text{ClF}_3$  rates, on the other hand have been reported at or near room temperature. The rate of reaction of  $\text{ClF}_3$  with  $\text{UF}_4$  has been reported at and below room temperature. Corresponding rates of  $\text{ClF}_3$  with  $\text{UO}_2\text{F}_2$  have been reported at temperatures a few tens of degrees above room temperature, with temperature dependence behavior providing the extrapolation to room temperature shown in Table 1 and Figure 1.

**Table 1. Reported or estimated rate constant, in units of  $\text{hr}^{-1}$  for gas-solid deposit removal reactions**

	$\text{F}_2$	$\text{ClF}_3$
$\text{UF}_4$	0.14 to 0.6 @ 280°C <sup>a</sup> 0.5 to 2.0 @ 320°C <sup>a</sup>	4 to 8 @ 21°C <sup>c</sup>
$\text{UO}_2\text{F}_2$	1.0 @ 540°C <sup>b</sup> 0.3 @ 360°C <sup>b</sup> 1.2 @ 400°C <sup>f</sup>	1.7 @ 165°C <sup>d</sup> 0.1 @ 90°C <sup>d</sup> (0.002 extrapolated to 25°C) <sup>d</sup> 0.22 @ 66°C <sup>e</sup> (0.03 extrapolated to 25°C) <sup>e</sup>

<sup>a</sup> (LaBaton 59a); <sup>b</sup> (Iwasaki 68); <sup>c</sup> (LaBaton 59b); <sup>d</sup> (Henrion 71); <sup>e</sup> (Harris 64);  
<sup>f</sup> (Iwasaki 64)

A few words are in order about the sources of rate data in Table 1. LaBaton examined the rates of reaction of powdered  $\text{UF}_4$  with  $\text{F}_2$  (LaBaton 59a) and  $\text{ClF}_3$  (LaBaton 59b). In both cases, there was evidence that the  $\text{UF}_4$  first was converted to  $\text{UF}_5$ , then more slowly reacted to form  $\text{UF}_6$ . The powder was 150 mesh (i.e., 0.105 mm particles). BET\* areas were measured ranging between 0.021 and 2.02  $\text{m}^2/\text{gm}$  and had a weak effect on reaction rate. The partial pressure of the fluorine ranged from 70 to 760 Torr, the rates quoted above being for 220 Torr. The reaction rate varied linearly with  $\text{F}_2$  partial pressure. The partial pressure of  $\text{ClF}_3$  in LaBaton's other study ranged from 39 to 74 Torr and within this narrow range, the rate also varied approximately linearly with partial pressure.

Of the  $\text{UO}_2\text{F}_2$  rate studies listed above, only Harris (Harris 64) worked directly with  $\text{UO}_2\text{F}_2$ . His experiments examined rates of reaction for  $\text{ClF}_3$  flowing across a shallow powder bed. Particle sizes and bed depth were not mentioned; BET areas were determined (6 and 11  $\text{m}^2/\text{gm}$ ); rates varied somewhat less than linearly with surface area. Partial pressures ranged from 5 to 103 Torr and had a less-than-linear effect on rate. The experimental temperature range of 66 to 177°C followed an

\* Brunauer-Emmet-Teller areas, a technique which measures the surface area of a material on a molecular scale.

Arrhenius\*\* behavior nicely, allowing extrapolation to room temperature with some degree of confidence. One should remember, however, the non-monotonic nature of the rate of  $\text{ClF}_3$  with  $\text{UF}_4$ .

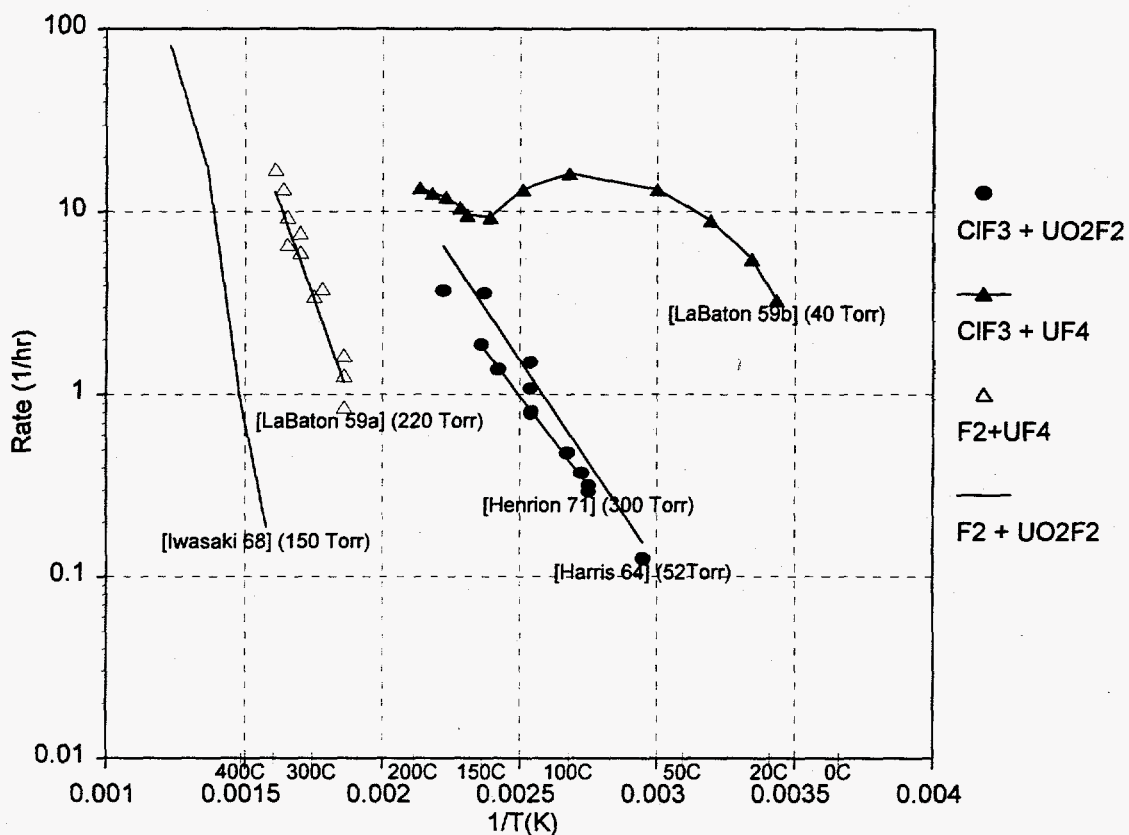


Figure 1 - Summary of reaction rates of  $\text{ClF}_3$  and  $\text{F}_2$  with reduced fluorides or oxyfluorides of uranium. Henrion 71 and Iwasaki 68 rates are actually for  $\text{UO}_2$ , which converts rapidly to  $\text{UO}_2\text{F}_2$  on the surface. Rate constants have been put into common units. Partial pressures of oxidizer are shown, but other factors (particle size; surface area) are not necessarily similar.

The remainder of the  $\text{UO}_2\text{F}_2$  studies examined fluorination of various uranium oxides (Iwasaki 64 --  $\text{F}_2 + \text{UO}_3$  and  $\text{U}_3\text{O}_8$ ; Iwasaki 68 --  $\text{F}_2 + \text{UO}_2$ ; Yahata 64 --  $\text{F}_2 + \text{UO}_2$ ; Henrion 71 -  $\text{ClF}_3 + \text{UO}_2$ ). In all cases, the reaction mechanism was found to involve first fluorination of the oxide to  $\text{UO}_2\text{F}_2$ , followed by a significantly slower process of fluorination of  $\text{UO}_2\text{F}_2$ .

Henrion's  $\text{ClF}_3 + \text{UO}_2$  study took place over the temperature range 90 to 165°C. The rate constant followed an Arrhenius dependence allowing extrapolation to room temperature with some degree of confidence. Total system pressure was not mentioned, but probably was about one atmosphere. Concentration of  $\text{ClF}_3$  had an approximate linear relationship with rate; the reported value is for 30 mole %  $\text{ClF}_3$ .

\*\* A common form for rate equations :  $\log k = A + B/T$   
where k is the rate, A and B are constants, and T is the absolute temperature.



The uranium oxides in the fluorine studies were in forms ranging from 0.1 to 2 mm grains or pellets. Generally, BET areas of the original oxide were determined, but had widely varying effects on reaction rate. The surface area of interest to us would be that of the  $\text{UO}_2\text{F}_2$ , which was not measured. Collectively, the uranium oxide studies were done at temperatures ranging from about 350 to 540°C and  $\text{F}_2$  pressures ranging from 80 to 400 Torr. Reaction increased approximately linearly with increasing  $\text{F}_2$  pressure. Temperature dependence within a given series of experiments gave reasonable Arrhenius-like behavior, but extrapolation to room temperature yields negligible rates.

In summary, though reaction rate information is not as detailed and comprehensive as we would like, the general reactivity trends in this system of reactants are apparent. Uranium fluorides are more prone to fluorination than is  $\text{UO}_2\text{F}_2$ , the latter reacting at perhaps ½ % to 2% the rate of the former, or requiring 100 to 150° higher temperature to achieve the same rate.  $\text{ClF}_3$  is as reactive at room temperature as  $\text{F}_2$  is at temperatures 250 to 300°C higher.

It would be very useful to know the deposit removal rates that might be expected in  $\text{ClF}_3$  treatment. The rate constants found in the literature can be applied to prospective MSRE treatment conditions, but the resulting predictions will be very uncertain due to unknown factors. At this writing, the chemical form of the plugs is unknown, let alone their physical distribution, morphology, and microscopic surface area. Nevertheless, for purposes of illustration and comparison, the following are offered. Erosion rate,  $dl/dt$ , can be estimated from the following:

$$dl/dt = r k f(P) f(A)$$

where  $r$  is the characteristic dimension of the material in a given study (grain size or pellet radius),  $k$  is the rate constant in that study (in reciprocal time units) computed at the MSRE treatment temperature,  $f(P)$  is a scaling factor to adjust the rate from the partial pressure in the literature study to MSRE treatment conditions, and  $f(A)$  is a scaling factor adjusting for differences between the microscopic (i.e., BET) area of the material in the literature study and that of the MSRE deposit. In the three literature examinations of most applicability (*LaBaton 59b*; *Henrion 71*; *Harris 64*), some pressure dependence information was provided, allowing calculation of  $f(P)$ . Limited or no information is provided to calculate  $f(A)$ , nor do we know the appropriate characteristics for the MSRE deposits, so we will take  $f(A)$  as equal to 1. We will use the values for  $k$  from Table 1 and  $r$  from the quoted pellet or mesh sizes: 0.1mm (*LaBaton 59a*) and 0.7 mm (*Henrion 71*). Harris did not state the particle size in his study; we will guess it as being 0.1 mm. Assuming treatment in MSRE takes place at 25°C at a partial pressure of 300 Torr  $\text{ClF}_3$ , then the calculated erosion rates will be:

$$\text{UF}_4 + \text{ClF}_3 : dl/dt = (0.1\text{mm}) (4/\text{hr}) (4) = 1.6 \text{ mm/hr} \quad (\text{using rate of LaBaton})$$

$$\text{UO}_2\text{F}_2 + \text{ClF}_3 : dl/dt = (0.1\text{mm}) (0.03/\text{hr}) (2) = 0.006 \text{ mm/hr} \quad (\text{using rate of Harris})$$

$$\text{UO}_2\text{F}_2 + \text{ClF}_3 : dl/dt = (0.7\text{mm}) (0.002/\text{hr}) (1) = 0.0014 \text{ mm/hr} \quad (\text{using rate of Henrion})$$

To reiterate, these are very speculative values, and furthermore, neglect depletion of  $\text{ClF}_3$  at the surface. Longitudinal erosion of a dead end plug many cm long could be a very slow process at these rates. Expansion of the cross sectional dimension of pores in a slightly permeable plug, however, at these rates can conceivably gain communication with adjacent volumes fairly expeditiously.

Diffusion-Limited Gas Transport: While the above rates are not very rapid, actual uranium deposit removal may be limited more by mass transport than by reaction rate. Upon initial

introduction of a reactive gas mixture to a section of piping containing a deposit, the initial rates will equal the values given above (or perhaps exceed them, if local reactive heating is significant). Quickly, however, the reactant gases will be depleted at the immediate vicinity of the surface, to be replaced with reaction products. The reaction rate thus will soon be reduced to a rate dictated by the mass transport of fresh reactant gas to the surface and of reaction products away from the surface.

In a near-ideal situation, a deposit (e.g., a coating on a pipe wall) would be subjected to a flow of reactive gas down the pipe. The typical distance for diffusional mixing would be a fraction of the diameter of the pipe; diffusion times would be fairly short, and the cleanup reaction relatively rapid. For forced flow through a slightly permeable plug, diffusion would not be a factor, as the characteristic dimension would be the diameter of the pores in the solid. The worst case would be that of a plug totally impeding flow in a long dead-end pipe. In that case, after the initial fill of the pipe with reactive gas, the characteristic distance for diffusion will be an ever increasing distance along the axis of the pipe (as  $\text{ClF}_3$  near the deposit is consumed) until this characteristic diffusion distance approaches the length of the pipe. If no other mass transport mechanisms intervene, diffusion times can be on the order of hours to days in a pipe several meters long.

To illustrate this, a one-dimensional model was developed to simulate the reaction of  $\text{ClF}_3$  with either a  $\text{UF}_6$  or  $\text{UO}_2\text{F}_2$  plug in a pipe of varying length. Appendix B contains a sample calculation and a more detailed description of the model. The general result, however, is that if the only mechanism of transport of reactant gases to the vicinity of a dead-end plug is diffusion, the effective rate of reaction will be limited to values equivalent to 0.1 to 0.5 mm/hr.

Other natural mechanisms may assist in gas mixing, thereby enhancing the effective deposit removal rate. Convection could be driven by two factors. One is that reactive heating will tend to raise the temperature at the reacting surface, allowing for the possibility of local thermal convection. Second, the density of the reactant gas mix and the product gas mix may differ sufficiently to initiate density driven convection. In the  $\text{ClF}_3$ - $\text{UO}_2\text{F}_2$  reaction, for example, the average gas molecular weights of reactant and product (for the reaction as written in Rxn-4, and ignoring inert diluents) are 93 and 163 gm/mole respectively. Either mechanism will promote gas mixing in the vicinity of a plug, damping out as material and thermal gradients equilibrate. The effect, of course, could differ greatly with the vertical orientation of the plug.

A reacting plug at the bottom of a vertical pipe would produce a denser gas near the plug, located below the less dense reactant gas, a stable situation that would not promote convection.

Diffusion rates can be increased by judicious selection of operational parameters. Minimizing the presence of unreactive diluents will allow more rapid diffusion. Safety considerations (discussed elsewhere in this report) dictate the need for some level of nonreactive diluents, however. At lower pressure, diffusion is more rapid (the mean free path of gaseous molecules is longer). On the other hand, the total quantity of reactive gas available will also correspondingly decline with pressure and reaction rates will probably decline as well.

Various means of forcing improved mixing can be envisioned. A positive flow, however small, (e.g., through a slightly permeable plug) will assist greatly where it can be achieved. For an impermeable plug, the typical method of attack is to simply introduce a batch of gas, wait a while, then evacuate it, for example to a holding tank, where it would mix fairly thoroughly. Normally such an evacuated batch of reactant gas is discarded, but if only a relatively small quantity of the reactant were consumed, the entire gas load could be repeatedly reintroduced then removed from the pipe. In such a scheme, mixing takes place outside the pipe, thereby finessing diffusional mixing

limitations. Pulsing the pressure (increasing it then decreasing it repeatedly without completely removing it from the pipe) would promote mixing by the shearing action of gas flow in the pipe (due to gas viscosity, flow will be more rapid in the center than at the walls of the pipe). It is likely that operational considerations will preclude the attempt to apply any of the more elaborate mixing schemes discussed here, but they are available if the treatment campaign evolves to warrant the extra effort they would entail.

Opening Potential Pre-existing Leaks: The point of introducing  $\text{ClF}_3$  is to more rapidly react solid uranium deposits, namely  $\text{UO}_2\text{F}_2$  or its derivatives and  $\text{UF}_4$  and its derivatives. Both  $\text{F}_2$  and  $\text{ClF}_3$  have the chemical potential to fluorinate any conceivable non-volatile uranium deposits to  $\text{UF}_6$ , but the rate of reaction of  $\text{ClF}_3$  is much greater than that of  $\text{F}_2$  at low temperatures. The efficacy of this from a deposit recovery standpoint was discussed above, but here one should point out that there is a possible short-term disadvantage in this.  $\text{UO}_2\text{F}_2$  is the reaction product formed when  $\text{H}_2\text{O}$  (e.g., from humid air) reacts with  $\text{UF}_6$ . Under the right condition, a leak from atmosphere to or from a  $\text{UF}_6$ -containing region can effectively self-seal with  $\text{UO}_2\text{F}_2$  reaction products. A deposit of  $\text{UO}_2\text{F}_2$  only slightly permeable to diffusion of  $\text{HF}$  and  $\text{H}_2\text{O}$  can form which blocks any further rapid in- or out-leakage. If such leaks have occurred, for example at valve bellows or diaphragms, at gaskets, welds, or solder joints, then introduction of  $\text{ClF}_3$  may remove the  $\text{UO}_2\text{F}_2$  plug, reopening the leak. For this reason, it is advisable to perform the first treatment of the system only under conditions in which the treated area is held below the outside ambient pressure. In such an event, any leakage that developed would be inward. Repair of such a leak might prove problematical, however, and could restrict later operation to subatmospheric pressures.

Radiolysis of  $\text{ClF}_3$ :  $\text{ClF}_3$  is fairly effective at reacting with  $\text{UF}_5$  and with  $\text{UO}_2\text{F}_2$  or its hydrates, but  $\text{F}_2$  and  $\text{ClF}$  are much less so.  $\text{ClF}_3$  is subject to radiolytic decomposition to form  $\text{F}_2$  and  $\text{ClF}$  (*Wendolkowski 53*), which at room temperature only very slowly recombine to produce  $\text{ClF}_3$ . It is possible that the radiolysis of  $\text{ClF}_3$  will render its reaction with  $\text{UO}_2\text{F}_2$  or  $\text{UF}_5$  deposits less effective than expected. This intuitively seems implausible, but could be evaluated with a little effort from literature studies on the subject. The coaddition of a small concentration of  $\text{F}_2$  to the treatment gas mixture should assist in recombination. It is also possible that radiolysis will actually assist in converting reaction products ( $\text{ClF}$  and  $\text{ClO}_2\text{F}$ ) back to  $\text{ClF}_3$ .

Utilization of  $\text{ClF}_3$ : Because of limitations of gas mixing, it is possible that only a small fraction of the  $\text{ClF}_3$  introduced to the system will actually react with the target deposits. The remainder must be disposed of or otherwise handled. Furthermore, the lower the utilization, the more  $\text{ClF}_3$  would have to be procured and on hand. Though  $\text{ClF}_3$  is expensive, material costs will be trivial compared to time costs and cost of the chemical traps used to dispose of the spent or discarded agent. There may also be thresholds for quantity of hazardous material on hand that will raise a safety issue. Using a scheme that promotes gas mixing could increase the utilization and minimize such problems.

Duration and number of treatments needed: An obvious issue in the project economics is the duration of a treatment, the number of treatments needed until successful cleanup is achieved, and the overall duration of the cleanup campaign. This is not answerable without a better understanding of many of the issues discussed in this report, and likely will not be known before some initial gas treatments are made and evaluated. Still, these questions are critical to the cost of the cleanup and perhaps the remediation effort as a whole, and should be considered as choices are made regarding where to spend effort on enhancement or improvement of the process, and where to simply accept a simpler, less efficient method.

## 2.2 GAS HANDLING

General handling needs and potential hazards —  $\text{ClF}_3$ : Similar to fluorine,  $\text{ClF}_3$  is a strong oxidizing agent as well as an acid gas, and consequently poses similar hazards. One difference between  $\text{ClF}_3$  and  $\text{F}_2$  is that the vapor pressure, while substantial, is much lower. The boiling point of  $\text{ClF}_3$  is  $11.8^\circ\text{C}$ , whereas that of  $\text{F}_2$  is  $-188^\circ\text{C}$  (near that of  $\text{N}_2$  and  $\text{O}_2$ ). At  $25^\circ\text{C}$ , the vapor pressure of  $\text{ClF}_3$  is about 1290 Torr (1.7 atm) (*Grisard 51*). The implications of this are that  $\text{ClF}_3$  can be readily stored and shipped in liquid form under its own pressure. Breach of a  $\text{ClF}_3$  container could result in spillage of liquid  $\text{ClF}_3$  (if the breach were below the level of the liquid). Any flammable material contacted by liquid  $\text{ClF}_3$  will likely spontaneously ignite. On the other hand, a breach above the liquid level (e.g., at a regulator or other gas withdrawal plumbing) would result in escape of gas, but not with a very high differential pressure. It would also tend to limit itself as the surface of the liquid in the cylinder cools by evaporation to its boiling point.

Either of these fluorinating agents (and several of their reaction products) can form a potentially explosive mixture with organic compounds or water when mixed in a condensed state. Such a condition might readily occur in a dry ice or liquid nitrogen cold trap in which water vapor or oil (e.g., backstreaming from a vacuum pump) and fluorinating agent (being pumped from a reaction system) were simultaneously frozen into the trap. In such a situation, an explosion may well result, commonly on warming the trap. Due to its high vapor pressure,  $\text{F}_2$  is not as readily condensible, and thus not as subject to this problem. In any case, cold trapping of  $\text{ClF}_3$  (and its reaction products), unless very carefully controlled, should be avoided.

The general handling and health hazards of  $\text{ClF}_3$  proper are very similar to those of  $\text{F}_2$ , in fact similar enough that the precautions taken in the RGR for handling the high  $\text{F}_2$  concentrations expected in the MSRE gas should by and large suffice for handling of  $\text{ClF}_3$ .

Reaction Products: An additional factor that complicates the use of  $\text{ClF}_3$  is that its plausible reaction products are more complicated and diverse than those of  $\text{F}_2$ . As indicated in Rxn 3 and Rxn 4, above, products will include  $\text{ClF}$  and  $\text{ClO}_2\text{F}$  and possibly  $\text{ClO}_3\text{F}$ , each of which has its own handling and behavior hazards, though they are generally similar to those of  $\text{F}_2$ ,  $\text{HF}$ , and  $\text{ClF}_3$ .  $\text{ClF}$ ,  $\text{ClO}_2\text{F}$ , and  $\text{ClO}_3\text{F}$  are acid gases and strong oxidizers, though they are less effective fluorinating agents than  $\text{ClF}_3$ .  $\text{ClF}$  and  $\text{ClO}_2\text{F}$  can further react with  $\text{UO}_2\text{F}_2$  or  $\text{UF}_6$ , albeit at slower rates than  $\text{ClF}_3$ . Should further reaction take place, these compounds eventually will be completely stripped of fluorine, producing  $\text{Cl}_2$  and possibly  $\text{ClO}_2$  if water of hydration is in excess.  $\text{ClO}_2$  rapidly reacts with virtually any material with a fluorinating potential stronger than  $\text{HF}$ , (including  $\text{ClF}$ ,  $\text{F}_2$ ,  $\text{ClF}_3$ , and  $\text{UF}_6$ ), so as long as some concentration of any of these materials is present, the reaction will effectively stop at the stage in which  $\text{ClF}$  and  $\text{ClO}_2\text{F}$  are the primary products.

To insure that  $\text{ClO}_2$  does not form in any significant quantity, a small proportion of  $\text{F}_2$  is often added to a  $\text{ClF}_3$ -containing treatment gas, particularly if the circumstances are such that the gas composition cannot conveniently be monitored during the treatment.

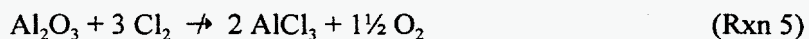
$\text{ClO}_2\text{F}$ ,  $\text{ClO}_3\text{F}$ , and  $\text{ClO}_2$  are all thermodynamically unstable relative to decomposition (to  $\text{ClF}$  and  $\text{O}_2$  in the case of  $\text{ClO}_2\text{F}$  and  $\text{ClO}_3\text{F}$ , and to  $\text{Cl}_2$  and  $\text{O}_2$  in the case of  $\text{ClO}_2$ ).  $\text{ClO}_2\text{F}$  and  $\text{ClO}_3\text{F}$ , however, are kinetically very stable, requiring temperatures above  $300^\circ\text{C}$  and  $450^\circ\text{C}$  respectively before the decomposition rate becomes easily measurable (*Heras 59; Gatti 60*).

An experimental study by Williams et al. (*Williams 97*) examined the behavior toward  $\text{ClF}_3$  of a chemical trap series simulating the RGRS system. Two tests were performed, one examining high

ClF<sub>3</sub> flow and concentration (approximating the maximum treatment concentrations and gas flow rates likely to be encountered) and the other at low flow and concentration (simulating low concentration treatments). ClO<sub>3</sub>F was observed leaving the alumina trap for much of the duration of the low flow run (approximately 10% of the incoming ClF<sub>3</sub> appearing as ClO<sub>3</sub>F). Reactive heating of the alumina (and consequently the trap temperature) under low flow conditions is relatively low, impeding the reaction of the more stable compounds such as ClO<sub>3</sub>F. This compound did not transit the molecular sieve trap, presumably being adsorbed or reacted. Under high flow conditions, ClO<sub>3</sub>F did not emerge from the alumina trap until shortly before breakthrough. ClO<sub>2</sub>F in neither case emerged from the alumina trap until near breakthrough. Neither ClO<sub>3</sub>F nor ClO<sub>2</sub>F emerged from the molecular sieve trap until ClF<sub>3</sub> had broken through the alumina trap.

Due to their kinetic stability, ClO<sub>3</sub>F and ClO<sub>2</sub>F pose no especial hazards other than being strong oxidizers. ClO<sub>2</sub>, on the other hand, can decompose explosively even at room temperature, particularly in the condensed state. Thus, its generation should be avoided. ClO<sub>2</sub>, however, is known to react rapidly with several of the potential fluorinating agents (ClF<sub>3</sub>; F<sub>2</sub>) including some that we would consider as reaction products (e.g., UF<sub>6</sub> and ClF). Thus, in the regions where any of these are present (e.g., in the MSRE piping system), it should not form in appreciable quantity, even when the ClF<sub>3</sub> is completely depleted locally. Only under circumstances where all of the fluorine atoms in these fluorinating agents are bound up as very stable fluorides (e.g., as AlF<sub>3</sub> or as HF in the alumina trap) is there a possibility of formation of significant quantities of ClO<sub>2</sub> or other chlorine oxides. In Williams' experimental series, ClO<sub>2</sub> was observed emerging from the alumina trap for just a few minutes part way through the trap consumption cycle. Concentrations were higher in the low flow experiment. In neither case did ClO<sub>2</sub> pass the molecular sieve trap (*Williams 97*).

As the treatment gas mix is removed from the system through the chemical trap system, additional reactions will take place. In the NaF trap, little should transpire, other than conversion of any reduced or hydrolyzed uranium compounds back to (NaF)<sub>2</sub>·UF<sub>6</sub>, which is desirable from the standpoint of recovery and conversion of uranium to its ultimate storage form. In the alumina trap, however, unreacted ClF<sub>3</sub> will tend to convert any UO<sub>2</sub>F<sub>2</sub> (the deposited form of U that has managed to reach the alumina trap) back to UF<sub>6</sub>. This UF<sub>6</sub> will then move downstream until it either encounters unfluorinated activated alumina or escapes the trap. ClF<sub>3</sub>, ClF, and ClO<sub>2</sub>F will all react with the activated alumina and its water of hydration to form AlF<sub>3</sub>, HF, Cl<sub>2</sub>, and perhaps HCl and ClO<sub>2</sub> or other chlorine oxides or hydroxides. Cl<sub>2</sub>, HCl and other chlorine-oxygen-hydrogen compounds may adsorb on the high surface area of unreacted activated alumina, but they are not likely to be completely consumed in a reaction analogous to the trapping of fluorine. The reaction:



will not occur because the aluminum oxide is much more thermodynamically stable than the chloride. Thus, in the trans-trap region of the RGRS, where in normal system operation no particularly reactive or hazardous gases were expected, we must now anticipate the possibility that Cl<sub>2</sub> and possibly HCl and chlorine oxides may be present. This raises some new operational concerns, including gas disposal and materials compatibility.

The possibility of ClO<sub>2</sub> or other unstable oxides in the trans-trap region of RGRS was considered sufficiently important that considerable effort was devoted to (a) determining experimentally circumstances in which it might appear in the RGRS system and the quantity that could appear, and (b) determining safe levels of ClO<sub>2</sub> and other oxides. The results of the experimental study (*Williams 97*) indicated that ClO<sub>2</sub> could indeed form in the alumina trap, but only under very restrictive conditions. ClO<sub>2</sub> appeared in the effluent from the alumina trap for a very brief

time partway through the trap consumption cycle (at about 50% of the  $\text{ClF}_3$  breakthrough time in one experiment and 75% in the other) The concentration of  $\text{ClO}_2$  in both experiments was fairly low. Most likely, it was formed directly from  $\text{ClF}_3$  (Cooper 72) interacting with excess water (formerly water of hydration in the alumina), which is known to emerge from the alumina trap late in its consumption cycle. No  $\text{ClO}_2$  was observed to pass the molecular sieve trap. A literature search and review on chlorine oxide flammability and explosivity was conducted and documented in letter format. The text of that letter is included as Appendix E. Recommended limits for action for  $\text{ClO}_2$  and  $\text{Cl}_2\text{O}$  are 2 mole % and 20 mole % in the average holding tank volume, respectively.

The general conclusions to be drawn from these two studies are that, while  $\text{ClO}_2$  seems unlikely to appear in quantities that will present any sort of hazard to RGRS, and  $\text{Cl}_2\text{O}$  mathematically can't present a hazard at presently contemplated  $\text{ClF}_3$  concentrations, both gases should be monitored in the RGRS off-gas stream (both are IR active and have known spectra). The "action" to be taken in the unlikely event that a limit is approached in the average holding tank composition could be any of the following: (a) cease withdrawing treatment gas through the trapping system until the gas is disposed; (b) dilute the holding tank gas with an inert gas; (c) wait for decomposition to reduce the concentration of the chlorine oxide.

Reactive heating: When an exothermic reaction is contemplated, the effect of reactive heating should be considered. There are two plausible locations for such heating in the MSRE/RGRS combined system. One is reaction at the deposit itself, and the other is reaction of  $\text{ClF}_3$  or its reaction products in the activated alumina trap. An implausible form of reactive heating would be reaction with metals used as a material of construction.

Reactive heating in the MSRE at the target deposits is not likely to be significant, since the reactants (a solid deposit and gaseous  $\text{ClF}_3$ ) will be, after the initial few seconds of reaction, separated by a boundary layer of reaction product gases. Deposits where there is good gas mixing (e.g., wall deposits away from a plug) have the large heat sink of the metal pipe to absorb heat of reaction. Reaction-induced temperature rises could be modeled or experimentally explored, but based on the long experience of using  $\text{F}_2$  and  $\text{ClF}_3$  for cleanup of such deposits in the uranium enrichment industry (and associated research programs), this is not likely to be an issue in the general case.

The chemical trapping system is designed to withstand the heat of reaction of  $\text{F}_2$  reacting with activated alumina at design flow rates and for fluorine concentrations up to about 70 mole %. The heat of reaction of  $\text{ClF}_3$  with activated alumina is, molecule for molecule, a bit higher than that of  $\text{F}_2$ , (largely because there are three F atoms per molecule rather than two). Using thermodynamic data from the JANAF Thermochemical Tables (JANAF 85), the heat evolved at room temperature in the reaction of  $\text{ClF}_3$  with alumina was calculated to be approximately 15% higher than the heat of reaction of the same quantity (on a mole basis) of  $\text{F}_2$  (see Appendix A). The maximum partial pressures to be used, however, will be lower than those of  $\text{F}_2$  in the MSRE off-gas by a factor that approximately compensates for the higher heat of reaction. The net effect is that heating in the trap will be very similar for MSRE off-gas and used treatment gases. Further, the alumina trap is instrumented to provide real-time readout of temperature at several positions within the trap. If the trap temperature appears to be rising to excessive levels, the gas flow (and consequently the reactive heat input) can be reduced as needed.

Reactive heating of metals used as materials of construction are not credible. Rapid reaction (fast enough to be self-sustaining by its own heat of reaction) can occur with  $\text{ClF}_3$  (as it can with  $\text{F}_2$  or  $\text{O}_2$ ), but only when the metal temperatures are very high, which usually requires a significant

ignition source or very finely divided, high surface area material. Unlike the two previous reactive heating scenarios, reaction with metals could tend to draw in additional oxidizer, as the products tend to be all solids, but the presence of an inert diluent impedes this by building up an inert diffusion layer at the reaction site. All in all, however, the MSRE does not appear to have any of the preconditions for rapid metal reaction.

Nuclear Criticality Safety: Any change in the RGR operation must be evaluated for its potential to alter nuclear criticality safety behavior. Use of  $\text{ClF}_3$  for the most part will only accomplish what it was hoped would be accomplished simply by sublimation and pumping, namely volatilizing solid deposits of uranium and pumping them in a controlled manner to the chemical traps. The quantity of  $\text{ClF}_3$  introduced into the system will be small in any given batch or operation, and it should be kept in mind that the Cl-35 isotope has a moderately high neutron absorption cross section, thus tending to suppress fission chain reactions.

Monitoring: For a variety of reasons, it will be desirable to monitor the gas composition during and after treatment. Most of the gaseous reactants and products can be monitored using the existing RGR on-line analytical equipment. Reactants will be  $\text{ClF}_3$  and secondarily  $\text{F}_2$ ; primary reaction products (those produced in the MSRE system) will be  $\text{UF}_6$ ,  $\text{ClF}$ ,  $\text{ClO}_2\text{F}$ ,  $\text{O}_2$ , and possibly small quantities of  $\text{Cl}_2$  and  $\text{ClO}_3\text{F}$ . If trace organics are involved, one might produce traces of  $\text{HF}$ ,  $\text{CF}_4$  and  $\text{COF}_2$ . Secondary products (those produced from reaction of the above gases with the alumina or molecular sieve traps) might also include  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}$ , or  $\text{HCl}$ , though probably only in trace quantities. Except for  $\text{O}_2$ ,  $\text{F}_2$  and  $\text{Cl}_2$ , all these gases are IR active and have known spectra.  $\text{ClF}$  may prove something of a problem as its single absorption band is weak and overlaps a much stronger absorption of  $\text{ClF}_3$ .

For mass balance purposes, it will be desirable to perform off-line spectral calibration tests on some or all of these gases. IR monitoring during a static exposure will not reveal anything particularly useful due to the very long time for diffusional mixing of gases. As a static charge of cleanup gas is withdrawn, however, IR monitoring of the gas could be helpful in revealing the nature of the non-volatile uranium deposits (e.g., if  $\text{ClF}$  appears, but no  $\text{ClO}_2\text{F}$  or  $\text{ClO}_3\text{F}$ , then the deposits are likely  $\text{UF}_4$  or  $\text{UF}_5$ ). This could also provide an indication as to the distribution of deposits in the pipe being treated. If a continuous flow-through exposure can be arranged, then monitoring of the exiting gas composition can provide a measure of the degree of completion of the treatment (i.e., if  $\text{ClF}_3$  reaction products continue to appear, then the reaction is still proceeding).

Monitoring of the reagent gas mix after passing through the traps will probably be necessary to determine the quantity and composition of gases that need to be disposed of. The main gas of concern is likely to be  $\text{Cl}_2$ , which is essentially IR-invisible. It is, however, an acid gas and may be detectable in the Sensodyne  $\text{F}_2$  or  $\text{HF}$  detectors, a point needs to be examined during preoperational testing. If the current cells prove insensitive to  $\text{Cl}_2$ , then a chloride version of the unit could be substituted for one or the other for the duration of the cleanup treatments, or the fluoroide version simply could be valved out for the duration of the  $\text{ClF}_3$  operation.

### 2.3 GAS DISPOSAL

In the RGR operation as originally planned, the chemical trap series was designed to remove all reactive gases from the gas stream, leaving an essentially benign mix to be vented to atmosphere. This trap series was designed to remove all reactive fluorides from the gas stream, and in operation to date, has done so effectively. When processing a  $\text{ClF}_3$ -containing gas mixture, the high-surface

area activated alumina and molecular sieve materials will have some adsorptive capacity for those species which do not directly chemically react. In a purged system, this means in practice that there will be a certain effective capacity for these gases, and that they will depart the trap only after some delay, an effect akin to gas chromatography. Possibly the combination of adsorption capacity and holdup delays will permit us to use the existing trapping system without modification. We must, however, allow for the fact that some reactive gases, most likely  $\text{Cl}_2$  and perhaps some non-fluorine-containing derivatives, will pass through the traps into the holding tank area. Thus, a new problem of gas disposal must be addressed. Several approaches might be taken in this event.

The simplest disposal method is to simply vent the gases. In this case the disposal issue devolves primarily into one of emission permitting. The quantities of  $\text{Cl}_2$  to be generated and needing to be vented, even under fairly incredible treatment schedules, are not large enough to be of regulatory concern (see Appendix C, Air Emission). This represents an administrative fix to the problem of use disposal of  $\text{ClF}_3$  products and is the approach that is currently planned for operation.

Other technical options are possible and were considered prior to the regulatory evaluation. Each would have varying advantages and disadvantages, requiring operational or hardware modifications.

Chlorine-containing gases can be chemically scrubbed in liquid or solid-bed adsorption systems. In laboratory experiments (*Williams 97*), it was demonstrated that the currently installed combination of activated alumina and molecular sieve will not completely trap all acid gases ( $\text{Cl}_2$  being the predominant hazardous gas passed) other trapping media could work better. The simplest technical fix would be to use different solid trapping media in the existing system. This could be done by changing the material in one trap, or perhaps by loading a trap with a layered combination of the current media and a new one (e.g., loading the alumina trap with 50% alumina followed by 50% different media).

Soda lime (a solid mixture of hydrated sodium and calcium oxides) may be able to chemically react the chlorine-containing compounds. The thermodynamic stability of the various potential reactants and products is favorable for conversion of  $\text{HCl}$ ,  $\text{Cl}_2$ , as well as any possible oxides to  $\text{NaCl}$  and  $\text{CaCl}_2$ . While the thermodynamics favor trapping of chlorine-containing gases, anecdotal experience suggests that this would not be effective at room temperature, and testing would need to be done to assure that the desired reactions occurred at a rate allowing complete removal at reasonable operational parameters for the existing MSRE trapping system. Other trapping media might also serve ( $\text{CaO}$ ;  $\text{CaCO}_3$ ;  $\text{MgO}$ ;  $\text{MgCO}_3$ ,...), but experience with such materials is much more limited and material availability in usable form is questionable. These factors would likely lead to requirements for more extensive development and testing than with soda lime.

Liquid scrubbing is commonly used to capture fluorides and chlorides. In such a system, a gas stream containing the gases to be removed is bubbled through an aqueous solution containing an alkaline solution, usually  $\text{KOH}$ . Chlorine and fluorine will go into solution as chloride and fluoride. Such a system would work in the MSRE, but would require substantial additional equipment and handling. Being substantially more complicated than the previously mentioned alternatives, it is not favored.

Recycle of the treatment gases is not a disposal method, but could reduce the quantity of gas requiring disposal. Recycle of  $\text{ClF}_3$  is technically feasible, but would require some hardware and procedural modifications. In its simplest form, recycle would amount to pumping the treatment gas through a  $\text{NaF}$  trap (to remove  $\text{UF}_6$ ) into a reservoir, then pumping it back to MSRE. Reaction



products would build up, but since it is likely that only a small proportion of the  $\text{ClF}_3$  introduced to the MSRE piping system will actually reach the vicinity of the pipe plugs and thus have an opportunity to react, several "uses" could be made of a single batch of treatment gas. A more elaborate form of recycle would involve regenerating  $\text{ClF}_3$  from its reaction products by addition of  $\text{F}_2$  and thermal processing. If the cost of using large quantities of  $\text{ClF}_3$  (which is mainly the cost of the associated trap consumption and disposal) prove to outweigh that cost of implementing a recycle scheme (time, hardware, and testing), this might be feasible. Early on, while treating the relatively small immediately accessible volumes of MSRE, there is little to be gained by recycling  $\text{ClF}_3$  over than simply disposing of each treatment batch. When treatment volumes get large, however, recycle may become more attractive. Consider that the original planned RGR project (prior to the discovery of the solid plugs) contemplated removal of approximately 3000 liters of gas. When most of the MSRE volume is accessible, each batch of treatment gas will be nearly this volume. The number of traps (alumina, not NaF) needed to capture the fluorinating agent will be comparable to the number originally contemplated for the entire campaign. At that point, some sort of recycle may be advisable on economic grounds.

## 2.4 MATERIALS COMPATIBILITY

Use of  $\text{ClF}_3$  and the generation of its associated reaction products raises a number of potential materials compatibility questions. For purposes of discussion, the MSRE and RGRS can be subdivided into several regions, each of which has its own set of planned or potential exposure conditions: (1) MSRE, especially the off-gas system; (2) High- $\text{F}_2$  areas of the RGRS (including the passivation cabinet where gas mixtures will be made up); (3) External areas, in particular the secondary enclosures where little or no exposure is expected, and where (if it were to occur) duration would be short and infrequent; (4) The chemical traps themselves; (5) RGRS beyond the activated alumina trap (i.e., beyond the point where fluorinating gases are present).

For the most part, materials that are recommended for service in  $\text{ClF}_3$  are the same as those recommended for service in  $\text{F}_2$  and  $\text{UF}_6$ . The best general materials of construction are nickel or high-nickel alloys (such as Monel). Aluminum, most stainless steels, copper and most of its alloys are also quite adequate, though they are less preferable at high temperatures.

MSRE off-gas system: The materials issues in the existing MSRE may be considered to fall into a few categories. Of primary interest are the off-gas piping and associated valving and instrumentation. Two other categories are the ACB and the fuel salt itself. Activated carbon can react rapidly with  $\text{ClF}_3$  (as it can with  $\text{F}_2$  under favorable conditions). There are no plans for introducing  $\text{ClF}_3$  to the ACB area intentionally and no reasonable prospects for this occurring accidentally, so this should not be an issue.

It is unlikely that  $\text{ClF}_3$ -containing gas will be directly and intentionally introduced to the chambers containing the fuel (or flush) salts early in the treatment campaign. During or after breach of the final plugs near the fuel flush tank or fuel drain tanks, however, such mixtures will be forced through the plugs and potentially expose the salt. The fuel salt consists of a mix of fluoride salts (Li, Be, Zr, and U, in order of concentration) which have been somewhat chemically reduced by radiolysis.  $\text{ClF}_3$  will not react with the parent fluorides. The thermodynamic stability of the fluorides is greater than that of the corresponding chlorides (see Appendix A). The main effect of  $\text{ClF}_3$  would be to refluorinate reduced sites in the salt to the extent it could access those sites.  $\text{F}_2$  should do the same. The fact that  $\text{F}_2$  (and later  $\text{UF}_6$ ) has built up in pressure in the gas phase indicates that such sites are inaccessible at the present conditions, presumably due to low diffusion or solubility of  $\text{F}_2$ .

in the salt. Most likely,  $\text{ClF}_3$  will be no more effective than  $\text{F}_2$  at refluorinating the salts, and will have little effect. Reaction rates with  $\text{UF}_4$  are such that it might convert reduced uranium fluorides to  $\text{UF}_6$ . It is likely to be able to do so, however, only for that portion of the salt immediately on gas-accessible surfaces. Generation of a trace of  $\text{UF}_6$  would not be surprising, though it would be difficult to distinguish this from conversion of plug material in the same general area. Williams et al. (Williams 97) recently exposed reduced, fluorine-depleted fuel salt to  $\text{ClF}_3$ , and observed no changes in either the composition of the gas over the salt (as determined by IR spectroscopy) or the weight or morphology of the fuel salt.

The portions of the MSRE that will be intentionally exposed to  $\text{ClF}_3$ -containing gas mixtures are the same portions that currently are exposed to high  $\text{F}_2$  concentrations. These areas are primarily constructed of stainless steels or Hastelloys. A review of safety documentation (Hedrick 97) listed these primary materials plus additional materials as indicated in Table 2.

Table 2. Generic materials of construction in the MSRE (Hedrick 97)

Hastelloy	Silver-plated nickel
Stainless steel	Phosphor bronze
Aluminum	Gold-plated copper
Monel	Nickel-plated brass
Copper	Brass
Solder	

All of the metal types listed are reasonably suitable for use in  $\text{F}_2$ - or  $\text{ClF}_3$ -containing atmospheres with the possible exception of "solder". Solders come in a very wide variety of forms with greatly differing compatibility for  $\text{F}_2$  and  $\text{ClF}_3$ . Still, exposure to  $\text{ClF}_3$  should be no worse than exposure to  $\text{F}_2$  at similar or higher concentrations. Morelock (Morelock 97; see Appendix D) conducted a review of the drawings and valve specifications in this region and concluded that all "wetted" parts of valves were made of stainless steel, brass, or Monel. Valve seats are either metal-to-metal seals or are made of Teflon [i.e., polytetrafluoroethylene (PTFE)]. These materials are satisfactory for service in  $\text{ClF}_3$  at room temperature (Farrar 60, Farrar 79, Farrar 80). Pawel independently came to the same conclusion in a review of MSRE compatibility issues related to  $\text{ClF}_3$  use (Pawel 97).

Within the region of interest in the MSRE off-gas system itself, PTFE is presently the only plastic known to be exposed to the  $\text{F}_2$ -containing gas. PTFE is as resistant to fluorination as any plastic, generally surviving extended service with no ill effects (though it can burn in  $\text{F}_2$  or  $\text{ClF}_3$  if some outside event initiates combustion). The fact that these specific components have been exposed for an extended period of time to high  $\text{F}_2$  partial pressures without incident makes the chance of ignition on exposure to  $\text{ClF}_3$  more remote.

RGRS - High  $\text{F}_2$  Region: Since that portion of the RGKS upstream of the chemical traps was designed for exposure to high concentrations of  $\text{F}_2$ , its materials of construction appear for the most part to be suitable for exposure to  $\text{ClF}_3$  and its reaction products. Certainly all the metals in the high- $\text{F}_2$  region will give satisfactory service in  $\text{ClF}_3$ .

Various components of the RGRS have elastomers in use as gasket or sealing materials. No organic is completely immune to reaction in high concentrations of strong oxidizers such as  $\text{ClF}_3$  or

F<sub>2</sub>. Contact with pure, high pressure or condensed oxidizer can result in ignition and burning. Their individual behavior will vary somewhat. Viton is a highly fluorinated polymer and relatively more resistant to halogens. As this report was in preparation, Viton O-rings in use in the RGRS IR system were found to fail (to slowly decompose) in high concentration ClF<sub>3</sub> service, though they had apparently survived similar F<sub>2</sub> levels. Where high ClF<sub>3</sub> concentrations are expected, Viton is being replaced with all-metal-sealed parts or with Chemraz®, an alternate material experimentally demonstrated to survive exposure to the conditions of interest (*Grindstaff 97*).

**RGRS - External Systems:** Areas that are expected to be exposed to low concentrations or for short duration on a very infrequent basis (e.g., ducting providing the secondary enclosure around the primary RGRS piping, which will be exposed only in the event of a leak; also personal protective equipment) may use elastomers that provide short-term resistance to these gas mixtures, e.g., Neoprene, Hypalon, Viton, or PVC. PVC and Neoprene are the recommended materials for protective equipment and clothing if exposure to low levels of F<sub>2</sub> is envisioned (probably due to a combination of its chemical resistance, favorable physical properties, and wide availability of protective equipment (*Farrar 60*)). Their behavior toward dilute and intermittent gaseous ClF<sub>3</sub> exposure should be similar. Hypalon seems to be a more recent substitute for Neoprene; while no direct information was found on its resistance, from its chemical structure one would expect it to behave similarly.

**RGRS Trapping systems:** The RGRS trapping system itself, exposed to ClF<sub>3</sub> (or to its reaction products) has been discussed in greater detail earlier. To briefly summarize, the NaF trap will pass F<sub>2</sub>, ClF<sub>3</sub>, and any Cl-containing reaction products. The activated alumina trap will react with F<sub>2</sub>, ClF<sub>3</sub>, ClF, and chlorine oxyfluorides, but will pass the incoming Cl as, primarily, Cl<sub>2</sub>. In addition to its primary function of trapping water and HF vapor that emerges from the alumina trap, the molecular sieve trap in experimental testing was found to trap any chlorine oxides or oxyfluorides that passed the alumina trap or convert them to chlorine and oxygen. In a post-experiment operation, an attempt was made to vacuum recover adsorbed species from the molecular sieve trap. Some ClO<sub>2</sub>, ClO<sub>3</sub>F and ClO<sub>2</sub>F were recovered, though the quantities were quite low (*Williams 97*), and in the case of the oxyfluorides, low relative to the amount of gas that had entered the trap in the course of the experiment.

**RGRS - trans-trap region:** Though we briefly mentioned the molecular sieve trap, the proper dividing line in terms of chemical environment is the reaction zone in the activated alumina trap. Upstream of this, a fluorinating environment prevails; downstream, the predominant reactive gas is Cl<sub>2</sub>, though H<sub>2</sub>O, O<sub>2</sub> and HF may play an important role.

Downstream of the activated alumina trap, one finds a short, unheated Monel tubing section, followed by a longer, heat-traced (to approximately 110°C) run of tubing which takes the gas to the molecular sieve trap. From the molecular sieve trap, the gas passes into one of two holding tanks. After a suitable time interval (to allow for Rn decay and for gas analysis), the gas is pumped through a local high-efficiency particulate air filter (immediately prior to which a small co-addition of ambient air is added to the stream). Past that point, the gas is ducted into the main building ventilation exhaust flow, which dilutes the RGRS exhaust gas by a factor of about 1000 and vents it out the building stack.

Without the addition of ClF<sub>3</sub> to the RGRS operation, the gas being vented consists primarily of He and O<sub>2</sub> (the reaction product of alumina and F<sub>2</sub>). The addition of ClF<sub>3</sub> to the operation adds Cl<sub>2</sub>, potentially at fairly high concentration, to this mix. Campbell reviewed RGRS drawings and materials specifications and found that the "wetted" portions of RGRS downstream of the molecular

sieve trap contain SS 304L, SS 316L, and aluminum, with neoprene and PTFE used as gaskets and valve seats, and with some valves using a silicone lubricant on shaft seals. Further downstream, the local high-efficiency particulate air filter is an acid resistant type with the filter medium consisting of Nomex-impregnated fiberglass and structural components consisting of galvanized steel, aluminum, and SS 409 (*Dumont 97*).

Pawel's analysis of this system (*Pawel 97*) concluded in general  $\text{Cl}_2$  exposure of the trans-alumina trap region presented no insurmountable difficulties.  $\text{Cl}_2$ , when dry, does not result in excessively rapid corrosion to the materials described, as evaluated on the basis of plausible number of exposure events and duration thereof. All the metals mentioned except aluminum are recommended for service in dry chlorine up to various temperatures ranging from 300 to 500°C. Higher corrosion rates apply for exposure to wet chlorine.

Aluminum (used in the pump body), can be considerably more sensitive to chlorine, and can be attacked at room temperature by wet chlorine, but is less vulnerable to dry chlorine. The holding tank region exposure will be to very dry chlorine (thanks to the molecular sieve trap), so the pump ought to hold up in service, but this may be a point of potential vulnerability.

The most sensitive area appears to be a 10" section of unheated Monel immediately past the alumina trap. Based on earlier experience, a partially (50%+) consumed alumina trap, subjected to high concentration  $\text{F}_2$  flow, will exhaust fairly high levels of water vapor, including a trace of HF. With the exit line cooled to room temperature, the concentration of water vapor emerging from the trap is sometimes high enough to result in condensation of a liquid phase. Replacing most of the  $\text{F}_2$  with  $\text{ClF}_3$  should not change this situation, but would result in the additional presence of gaseous  $\text{Cl}_2$  in this region. This certainly would count as a "wet- $\text{Cl}_2$ " environment, and Pawel indicates that though high-nickel alloys such as Monel are more resistant to corrosion than many other alloys, this is an environment in which rapid corrosion might be expected. Without direct experimentation, this can't be rigorously quantified, but guidance from literature suggests that continuous exposure corrosion rates on the order of a few mils/day could be experienced. One would not want to subject the unheated portion of the exit line from the activated alumina trap to more than a few days of continuous exposure to these conditions if these corrosion rates truly apply. The duration of exposure to potentially high-corrosion rate conditions will be on the order of 10 to 30 minutes per trapping event, and that only during that portion of the trap's lifetime in which significant levels of water are being evolved (say from about 50% consumption to termination of use of the trap at 75% to 90% consumption). HF exiting the trap could, absent  $\text{Cl}_2$ , also induce high corrosion rates should a liquid phase form. It is unknown whether any synergism might further accelerate corrosion in a wet HF and  $\text{Cl}_2$  environment (*Pawel 97*).

The combination of high corrosion rates but short exposure duration (followed by inert gas purging, which should remove the liquid phase as well as the corrosive gases) leads to the conclusion that this section of tubing should survive several trapping cycles. The prudent course is to remove and examine the unheated section of tubing the first time the alumina trap is changed out. Examination after actual experience should give a much better idea of the magnitude of corrosion and provide a better basis of routine change out of this part. Such an examination and maintenance/replacement program should prevent leakage in this part of the system. It should be noted, however, that the consequences of leakage are not severe since this section is downstream of the traps and would leak to a contained ventilated area of the RGRS.

The vacuum pump in the holding tank area has an aluminum body. Aluminum, if its protective oxide coating is breached, can react with  $\text{Cl}_2$  to form  $\text{AlCl}_3$ , which has a moderate vapor pressure and

is not protective. Materials literature examined by Pawel, however, suggests that dry  $\text{Cl}_2$  at room temperature (less than perhaps 0.1%  $\text{H}_2\text{O}$ ) should not unduly attack the aluminum of the pump, particularly considering the relatively short duration of exposure (*Pawel 97*).

Neoprene (polychloroprene, to give its chemical name) is a partially chlorinated hydrocarbon polymer. In RGRS, it is used in the diaphragm of the vacuum pump in the holding tank area. Neoprene is not ideal for  $\text{Cl}_2$  service. Some sources do not recommend it while others indicate that it is acceptable at room temperature. "Acceptable" is a sufficiently vague term that these statements may not be literally contradictory. Should the pump diaphragm fail, the pump will not function properly and conceivably could leak gas to (or from -- depending on the internal pressure) the pump's secondary enclosure. The short duration exposure to dry  $\text{Cl}_2$  is a factor in favor of allowing use of Neoprene. If RGRS operations confirm high concentrations of  $\text{Cl}_2$ , the vacuum pump should receive periodic inspection and preventive maintenance.

PTFE is used in valve seats in the holding tank area. It has no compatibility problems relating to exposure to  $\text{Cl}_2$ .

IR system components must withstand the full range of environments discussed, though the most severe in testing has proven to be the wet  $\text{Cl}_2$  gas immediately past the activated alumina trap. The sensitive component is the IR window, which is made of ZnSe. This material will withstand high  $\text{ClF}_3$ ,  $\text{UF}_6$  and dry  $\text{Cl}_2$  environments for an adequate period of time, but moisture mixed with  $\text{ClF}_3$  or  $\text{Cl}_2$  causes window degradation which quickly renders them opaque. There does not seem to be a convenient cure for this, but the necessary on-line analytical tasks of RGRS operation can be done without subjecting the IR system to these adverse gas mixtures.

To summarize the materials compatibility evaluations, changes in the chemical environment brought about by use of  $\text{ClF}_3$  create a few new areas of concern, but these manifest themselves as a possible need for increased maintenance. The system components more sensitive to the altered environment (one section of tubing, and the RGRS vacuum pump), should they fail, will primarily result in leakage of already-trapped gases into secondary ventilation enclosure, where there is no possibility of personnel exposure to hazardous gases.

### 3. SUMMARY

#### 3.1 A GENERAL SEQUENCE FOR $\text{ClF}_3$ TREATMENT

Integrating all of the above considerations, we can formulate a general sequence for a  $\text{ClF}_3$  treatment operation. Variations are of course possible, but the approximate course of treatment and major activities would be:

1. Make up the treatment gas mix of  $\text{ClF}_3 + \text{F}_2 + \text{inert (He)}$ . The initial treatment to a region previously unexposed to  $\text{ClF}_3$  should use a relatively low concentration of oxidizers, say 5%  $\text{F}_2$  and 5%  $\text{ClF}_3$ , in case there are high-reactivity deposits in the system. Routinely, the gas mixture would consist of a higher concentration (limited by safety analysis restrictions on the concentration or total quantity in the system), perhaps 30 to 50%  $\text{ClF}_3$ , 5%  $\text{F}_2$ , and the balance, He. The quantity made would be determined by the volume of the MSRE off-gas system to be treated.
2. Evacuate the region of the MSRE off-gas piping to the degree possible, just as in any normal gas removal operation of RGRS.
3. Introduce the treatment gas into this region of the MSRE off-gas system. The first few treatments should probably be at a total pressure below 1 atm, and the system monitored for the appearance of leaks induced by  $\text{ClF}_3$  cleanup of  $\text{UO}_2\text{F}_2$  "self-sealed" deposits. At pressures below 1 atm (absolute), MSRE gas flow through the plugs will be from the untreated area into the treated volume so, at best, surface reaction of plugs can be expected. Later, treatment gas pressures higher than the trans-plug MSRE pressures can be used, allowing limited flow of the treatment gas through the porous plugs. Ultimately, when alternate gas introduction points are available and access can be obtained to both sides of a plug, treatment gas flows can be increased by using higher pressure differences. In the second and third flow modes, treatment gas penetrating the plugs ought to erode the walls of the gas passages, and increase the conductance of the plugs allowing more rapid gas flow in a positive feedback process whose rate will be limited by the slower of the reaction rate of  $\text{ClF}_3$  with the deposit or the mass transfer rate of  $\text{ClF}_3$  to the plug.
4. Allow gas to react for appropriate length of time. For a static treatment, the point of diminishing returns will probably be reached in a few hours. For flow-through methods, the duration of treatment will be governed more by logistic and system volume considerations.
5. Remove the treatment gas from MSRE through RGRS traps, trapping  $\text{UF}_6$  on NaF, and reacting fluorinating agents with the activated alumina.
6. During gas removal, monitor gas being removed via IR. Monitoring gas concentrations as a function of time will give the best initial indication of the type of deposit that is being attacked. The quantities of  $\text{UF}_6$  produced will also provide a measure of the progress made at deposit removal. The degree of depletion of  $\text{ClF}_3$  will give a rough indication of the degree of localization of deposits within the system. In addition to IR analysis, the flow characteristics of the system should also be analyzed. Change in gas conductance of a plug is a direct measure of the progress made at gaining communication with other sections of MSRE.
7. Off-gas handling - Gas passed through the trapping system will be held (as before) for a period of time to allow gas analysis and decay of Rn and prompt daughter products. Current plans are to then vent this gas through the building ventilation stack.

The above steps can be repeated, with variations as needed until either success is achieved or it is deemed that the treatments have done all they profitably can. A minimal goal of the treatment process is the attainment of rapid flow communication to areas now blocked by slightly permeable plugs. There is every reason to expect that this can be achieved. Attaining communication through plugs that are completely impermeable may be much more difficult. There is, at present, no concrete proof of such plugs, but our characterization of plugs beyond those most immediately accessible is very poor. Removal of all U from the off-gas piping is technically possible, but to be practical would probably require some modification of the treatment scheme described that involved repeated cycling of gas in a continuous flow through the region containing deposits.

### 3.2 SUMMARY OF MOST CRITICAL ISSUES

A large number of issues and lesser considerations have been discussed in this report. Many of these issues have been resolved, in some cases by analysis and in other cases by experimentation or testing. Some issues remain open and will require in-process monitoring (or substantial delays for off-line testing). The issues perceived as most critical either at the inception or completion of this report, along with their current state of resolution, are:

1. Treatment efficacy — this remains unanswered in an absolute sense, but based on literature reports of chemical reaction rates and computational mass transport analysis, it appears that the deposit conversion rates should be rapid enough to allow regaining communication with inaccessible areas of the MSRE off-gas system.
2. Reactive heating — Relatively low reaction rates, low mass transport rates, and diffusion barriers imposed by reaction products and inert gas diluents render reactive heating of deposits an apparent nonissue. Reactive heating of the activated alumina trap will occur, but not to a substantially different degree than that which already exists with  $F_2$ .
3. Materials Compatibility — In a fluorinating environment,  $ClF_3$ 's effect on most materials of construction in use in MSRE or RGRS is substantially the same as that of  $F_2$ . Some elastomer material changes have been made motivated by test results on auxiliary systems of RGRS. Certain areas of RGRS (past the uranium-containing region) are potentially more vulnerable to corrosion or material degradation in the altered environment (activated alumina trap exit tube; Neoprene diaphragm of RGRS vacuum pump) and should be monitored carefully in shakedown tests and early operations, with planned maintenance or redesign contemplated if significant degradation is actually observed.
4. Gas disposal —  $ClF_3$  thermodynamically ought to react the activated alumina to  $AlF_3$ , producing an off-gas mixture of  $O_2$  and  $Cl_2$ . Experimental testing has confirmed this. Another possibility was formation of (unstable) chlorine oxides such as  $ClO_2$ . Experimental testing demonstrated that  $ClO_2$  only appeared very briefly and at low concentrations. A literature review established concentration limits for the presence of  $ClO_2$  in the RGRS off-gas which appear unlikely to ever occur, but which will be checked via on-line gas analysis.  $Cl_2$  is the primary product of  $ClF_3$  reaction with alumina. In the quantities contemplated, it can be vented with the RGRS off-gas.
5. Fuel salt effects — An experimental exposure of radiolytically reduced fuel salt to  $ClF_3$  showed no observable effect. Since the fuel salt containing areas are blocked from treatment gas input points by multiple plugs, there is little likelihood of any substantial exposure early in the treatment campaign in any case.

#### 4. CONCLUSION

Non-volatile deposits found to plug portions of the MSRE off-gas system are almost certainly reduced uranium fluorides or uranium oxyfluoride. Treatment with  $\text{ClF}_3$  is a non-intrusive method capable of at least partial removal of these deposits. The efficacy of deposit removal at room temperature is not likely to be rapid, however. Reaction rates are low, and mass transport limitations due to diffusion and flow will further limit the potential rate of deposit reaction. From a materials compatibility standpoint,  $\text{ClF}_3$  is usable with little risk to MSRE (beyond what already is borne by the presence of  $\text{F}_2$ ). Some issues or uncertainties arise with use of this material, as neither MSRE nor the RGRS system were initially designed and planned with  $\text{ClF}_3$  use in mind. These issues have been discussed in this report. Other than efficacy of treatment, the main issues revolve around the chlorine-containing reaction products of  $\text{ClF}_3$  upon its reaction with the activated alumina trap. The issue of  $\text{ClO}_2$  generation appears to have been laid to rest by a combination of experimentation and literature research on safe limits of that gas. Issues related to the formation and disposal of  $\text{Cl}_2$  are adequately resolved. Related materials compatibility issues in involving  $\text{Cl}_2$  and RGRS post-trap regions retain some uncertainties, and will require monitoring during testing and operation.



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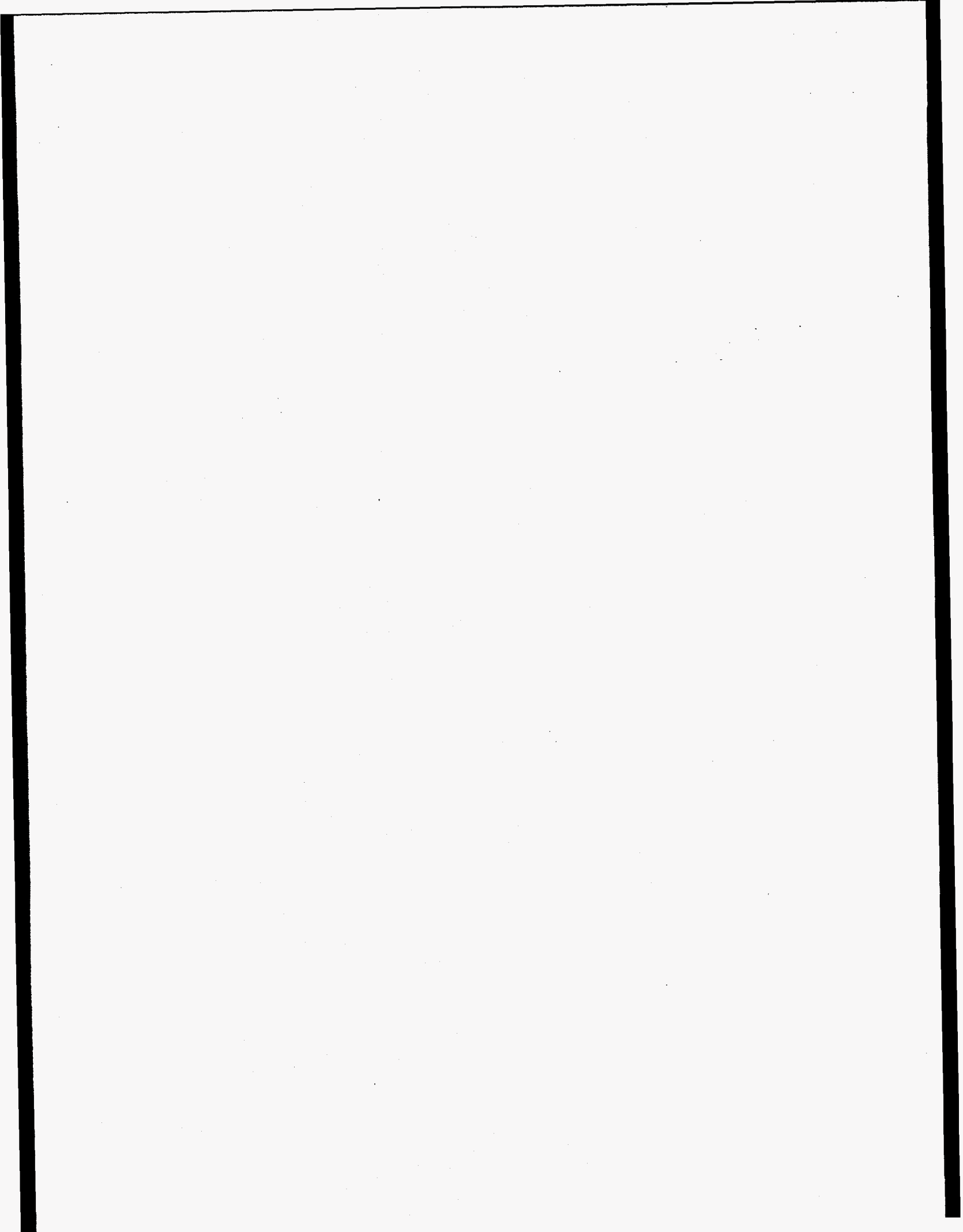
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**APPENDIX A**

**THERMODYNAMIC STABILITY CALCULATIONS**



## Thermodynamic Stability Calculations

Some guidance as to the chemical behavior of the MSRE and RGRS on exposure to  $\text{ClF}_3$ -containing treatment gases can be obtained from thermodynamic calculations. Such calculations indicate the equilibrium chemical state of a system within the limits of the chemical species considered and the accuracy of the thermodynamic data used. The equilibrium state is that which will be achieved if reaction rates are fast enough to allow it to be reached (a condition often not satisfied in practice).

Calculations reported in this section used the computer program SOLGAS (*Trowbridge 95b*) along with thermodynamic data largely from JANAF (*JANAF 85*) compilation (data for some of the listed species, unavailable in JANAF, were taken from locally developed estimates, but no such species proved important in the results shown here).

**Reduced Fuel Salt:** A calculation was run to validate our intuitive notion that  $\text{ClF}_3$  exposure to reduced fuel salts would not result in formation of chlorides in preference to fluorides, so long as all the fluorine content of  $\text{ClF}_3$  were not consumed. Low diffusion rates in the salt should prevent accessibility of the bulk of the salt except in a small surface region. The calculation depicted in Figure A-1 places the initial fluorine deficit in the form of  $\text{UF}_6$ , but allows the presence of the reduced zirconium fluoride  $\text{ZrF}_3$  as well. Chlorides of all the salts are included as possible reaction products. The various salts are treated as members of an ideal (solid) solution. This is not the true state of affairs, of course, and represents an approximation.

The initial quantity of  $\text{ClF}_3 + \text{F}_2$  is more than sufficient to satisfy the anion deficit of the salt. The results, as expected, show that the anion deficit is removed by formation of fluoride, not chloride, salts. The calculation also predicts that uranium would be removed from the salt, entering the gas as  $\text{UF}_6$ . In practice, these results should be interpreted as applying only to a probably very thin surface layer of the salt in equilibrium with the gas, the bulk being inaccessible to  $\text{F}_2$  or  $\text{ClF}_3$  at these temperatures.

An experimental exposure of radiolytically reduced fuel salt to  $\text{ClF}_3$ , reported elsewhere (*Williams 97*) produced no overt changes to the salt.

**Reactive Heating of Trap Material:** One issue in the use of  $\text{ClF}_3$  with the existing trapping system is that of the degree of reactive heating that will occur in the activated alumina trap relative to that expected and experienced with trapping of high-concentration  $\text{F}_2$  gas mixtures. A series of thermodynamic calculations was run to examine this question. The general scenario used calculated the equilibrium gas composition and heat evolution under isothermal (i.e., constant temperature) and adiabatic (i.e., fully insulated) conditions for 10 gm-moles of activated alumina reacting with one gm-mole of a gas mixture containing 30 mole%  $\text{F}_2$  or  $\text{ClF}_3$ . Thermodynamic properties for activated alumina were not available, so the activated alumina was approximated as a mixture of 75% gamma-alumina and 25% boehmite, a combination that has the approximate degree of hydration of the prepared A-201 pellets used in MSRE. Alumina in this scenario is in excess, so the adiabatic temperatures do not represent the maximum temperatures that could be achieved in a perfectly insulated reactor using exact stoichiometric proportions of reactants. Figure A-2 displays the output from one such run (adiabatic case in which  $\text{ClF}_3$  is the oxidizer). Table A-1 summarizes the results of all the runs. These calculations predict that (on a per-mole basis)  $\text{ClF}_3$  will generate about 15% more heat than  $\text{F}_2$  in an alumina trap.

**Table A-1. Heat evolved from 1 mole of gas (30 mole% oxidizer, balance He) reacting with 10 moles activated alumina (thermodynamic computation)**

Oxidizer	T (°C)	Heat Evolved (kJ)
ClF <sub>3</sub>	25	157 (isothermal)
F <sub>2</sub>	25	137(isothermal)
ClF <sub>3</sub>	144	156(adiabatic)
F <sub>2</sub>	128	136(adiabatic)

Thermodynamic Equilibrium Computation

Data File: msr\_clf.dat

Results File: g:msre02.out

SOLGAS Ver. 4.00.h.1

10/8/1996

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	Initial	Final	Heat Changes
T =	300.000	300.000 K	Pre-Heat : 0.000 kJ
P =	1.000	1.000 bar	Reaction : -28.637 kJ
V =	0.000	0.000 liters	Total : -28.637 kJ

	Initial Qty (moles)	Final Qty (moles)	Pressure (bar)
Cl2(g)	0.000000D+00	0.123310D-11	0.111060D-11
ClF(g)a	0.000000D+00	0.150000D-01	0.135141D-01
ClF3(g)	0.100000D+01	0.985000D+00	0.887387D+00
F2(g)	0.100000D+00	0.168238D-09	0.151511D-09
UF6(g)	0.000000D+00	0.110000D+00	0.990991D-01

	Initial Qty (moles)	Final Qty (moles)	Mole Fraction
BeCl2(c)	0.000000D+00	0.774664D-94	0.775440D-96
BeF2(c)	0.350000D+02	0.350000D+02	0.350350D+00
LiCl(c)	0.000000D+00	0.259286D-35	0.259545D-37
LiF(cr)	0.640000D+02	0.640000D+02	0.640641D+00
UF3(s)	0.100000D-01	0.140275D-94	0.140415D-96
UF4(s)	0.100000D+00	0.296758D-32	0.297055D-34
UF4.25(s)	0.000000D+00	0.978743D-27	0.979723D-29
UF4.5(s)	0.000000D+00	0.289197D-21	0.289486D-23
UF5(b)	0.000000D+00	0.676372D-11	0.677049D-13
ZrCl3(c)	0.000000D+00	0.250231-201	0.250481-203
ZrCl4(c)	0.000000D+00	0.664610-165	0.665276-167
ZrF3(c)	0.000000D+00	0.712687D-80	0.713401D-82
ZrF4(c)	0.900000D+00	0.900000D+00	0.900901D-02
UF6(cr)	0.000000D+00	0.000000D+00	

*Figure A-1: Thermodynamic calculation of equilibrium of MSRE salt (fluorine-depleted) reacting with ClF<sub>3</sub> (a check for relative chloride vs. fluoride stability).*

Thermodynamic Equilibrium Computation  
 Data File: trapheat.dat  
 Results File: trapheat.out

SOLGAS Ver. 4.00.h.5  
 1/03/1997  
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	Initial	Final	Heat Changes
T =	298.150	298.150 K	Pre-Heat : 0.000 kJ
P =	1.000	1.000 bar	Reaction : -156.938 kJ
V =	24.790	26.649 liters	Total : -156.938 kJ

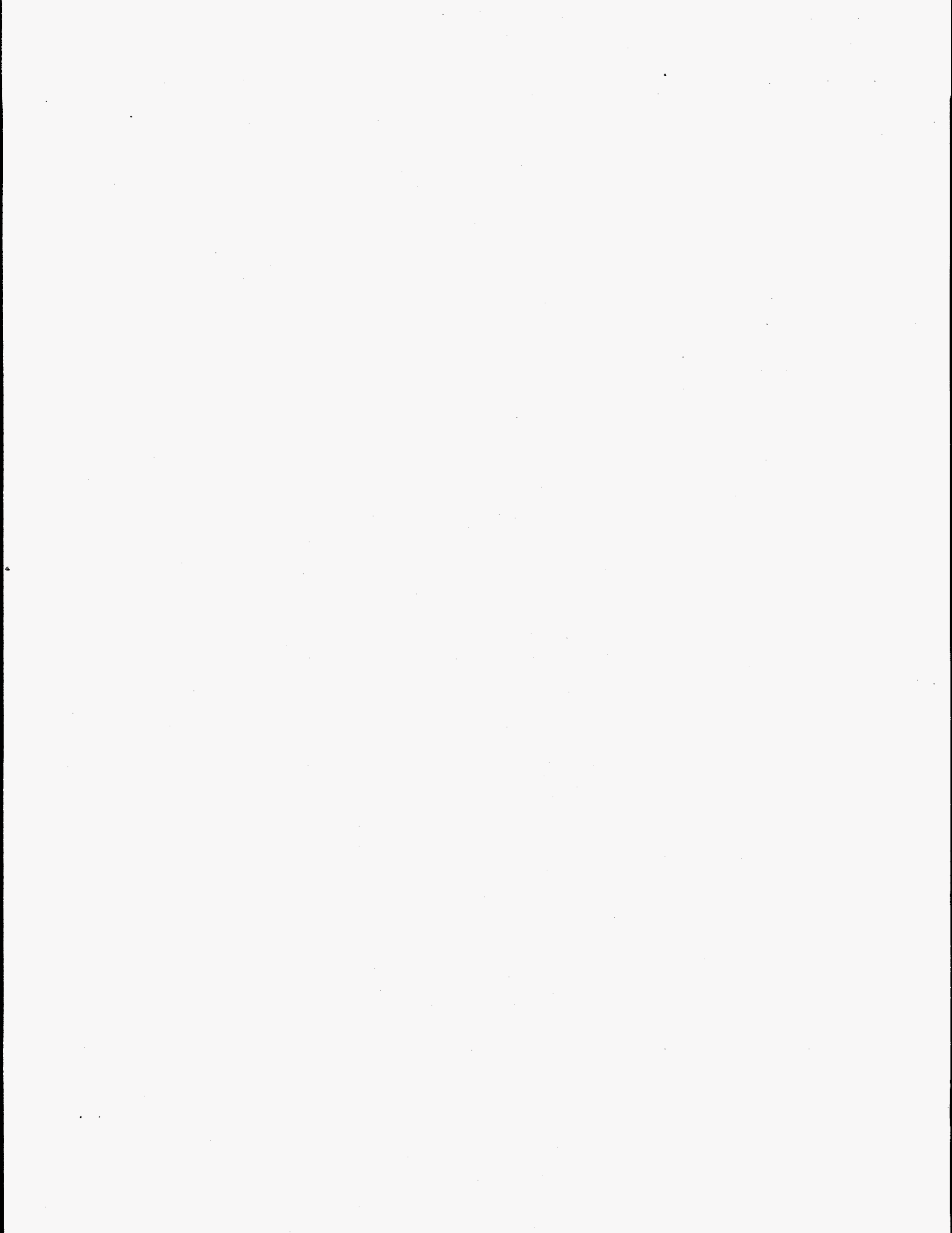
	Initial Qty (moles)	Final Qty (moles)	Pressure (bar)
He	0.700000D+00	0.700000D+00	0.651163D+00
ClF3(g)	0.300000D+00	0.153661D-93	0.142941D-93
F2(g)	0.000000D+00	0.739785D-76	0.688172D-76
Cl2(g)	0.000000D+00	0.150000D+00	0.139535D+00
ClF(g)a	0.000000D+00	0.393279D-29	0.365840D-29
ClO2F(g)	0.000000D+00	0.939938D-42	0.874361D-42
ClO3F(g)	0.000000D+00	0.284750D-48	0.264884D-48
HCl(g)	0.000000D+00	0.106478D-06	0.990495D-07
HClO(g)	0.000000D+00	0.630023D-13	0.586067D-13
HF(g)	0.000000D+00	0.626891D-13	0.583155D-13
O2(g)	0.000000D+00	0.225000D+00	0.209302D+00
H2O(g)	0.000000D+00	0.158061D-06	0.147034D-06
ClO2(g)	0.000000D+00	0.311774D-22	0.290022D-22
Al2O3(gamm)	0.750000D+01	0.735000D+01	
Boehmite	0.250000D+01	0.250000D+01	
AlF3(alpha)	0.000000D+00	0.300000D+00	
ClF3(l)	0.000000D+00	0.000000D+00	
ClO2F(l)	0.000000D+00	0.000000D+00	

Figure A-2: Sample calculation from set which examines the heat generation during reaction of activated alumina with ClF<sub>3</sub> and F<sub>2</sub>. This run examined the isothermal (room temperature) reaction of 30 mole % ClF<sub>3</sub>.



**APPENDIX B**

**DIFFUSION LIMITATION ON REACTION RATES**



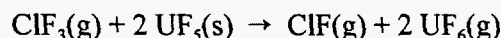
### Diffusion Limitation on Reaction Rates

Gas reaction of a plug at the end of a dead end line without some sort of gas mixing will almost surely suffer limitations due to depletion of the reactant gas in the vicinity of the plug. Reaction rates will then be limited to the rate of diffusion to the site of reaction. To obtain insight into the importance of diffusion limitation of reaction rates, a simple one-dimensional finite-element model was developed. The model computes multicomponent gas-phase diffusion down a pipe to a reacting surface, i.e., a rough simulation of  $\text{ClF}_3$  treatment of a plug in a pipe when there is no mass transport other than (a) addition of  $\text{UF}_6$  into the gas at the "plug" end of the pipe and (b) conversion of reactant gas to product gas(es) and (c) diffusion. In this model, the reaction rate constant at the surface is assumed to be infinite. Incorporation of a reaction rate into the program would be quite simple if a reliable rate could be obtained, but this simulation is an examination of diffusion limitation on reaction rate only.

The model assumes the following general physical configuration:

- (1) A pipe with a cross-sectional area of  $1 \text{ cm}^2$  and a length specified by the user.
- (2) The pipe is closed at one end by a deposit of  $\text{UF}_5$  or  $\text{UO}_2\text{F}_2$ .
- (3) The pipe is open at the other end to a large reservoir.

It is assumed that gas in the large reservoir is completely mixed, but that mixing in the pipe, which is subdivided into a number of volume elements, occurs only by diffusion between adjacent elements. Gas in the final volume element (the one at the plug) is assumed to completely react per the appropriate equation below:



or



since the number of moles in this volume element changes as the reactions proceed, some additional transport occurs by expansion of gas at the site of reaction.

Gases considered in the model are  $\text{ClF}_3$ ,  $\text{ClF}$ ,  $\text{ClO}_2\text{F}$ , He, and  $\text{UF}_6$ . Diffusion is calculated by standard Fick's law method, with diffusion coefficients estimated per equations given in Skelland (*Skelland 74*), and molecular interaction and collision cross section parameters taken from that book (He;  $\text{UF}_6$ ) or estimated ( $\text{ClF}_3$ ,  $\text{ClF}$ , and  $\text{ClO}_2\text{F}$ ) based on parameters for similar compounds. Known and recognized limitations of the model include uncertain diffusion constants; ignoring the chemical reaction rate constant; ignoring reactive heating; ignoring convective mixing. Convective mixing (which should vary greatly with variation in the orientation of the pipe) might to occur due to two competing factors: gas density change and local heating at the reaction site.

The model's output consists of a time history of the gas composition in each volume element. Two specific output values of operational interest are termed "U up" and "U out". These give, respectively, the number of grams of U put into the gas phase (in the pipe or out its end) and the

grams of U that have diffused all the way out of the pipe. Figure B-1 shows this output for three different scenarios. The conditions of the scenarios were:

T = 25 °C

P = 1.002, 0.501 or 0.2 atm

Gas composition = 50% ClF<sub>3</sub>, 50% He (mole percent)

length of pipe = 1 meter

cross section of pipe = 1 cm<sup>2</sup>

From the graph one can see that while a diffusion gradient is established from the reaction site to the end of the 1 meter pipe (over the course of about 4 hours at 1 atm, less for lower pressure), the reaction follows the expected square-root-of-time dependence, after which the rate is linear as determined by the diffusion rate along a 1 meter pipe. Transport of U out of the pipe is most rapid for lower pressures, but total U raised (including that still in the pipe) is higher for the higher pressures. Though the rate falls off as the diffusion gradient builds and spreads, the average diffusion limited rate over the first hour of reaction for these three cases is as shown in Table B-1 where the erosion rate is computed from an approximate density for UF<sub>5</sub> of 6 gm/cc. Runs for reaction of UO<sub>2</sub>F<sub>2</sub> gave diffusion limited rates approximately 40% as large for equivalent conditions, the difference being due to a combination of the greater quantity of ClF<sub>3</sub> needed to raise a given quantity of UF<sub>6</sub> and the smaller gas volume increase.

**Table B-1. Average diffusion limited rate of U recovery in one hour  
for conditions stated in the text**

Total P (atm)	U raised (gm)	UF <sub>5</sub> converted (gm)	Erosion (mm/hr)
1.02	0.11	0.16	0.30
0.51	0.07	0.10	0.17
0.20	0.05	0.07	0.12

Comparing these diffusion limited erosion rates with the approximate erosion rates derived from chemical reaction rate constants, we can conclude that for recovery of UF<sub>4</sub> or UF<sub>5</sub> deposits (about 1.6 mm/hr), the recovery may well be limited by diffusion rather than reaction rate. For UO<sub>2</sub>F<sub>2</sub> recovery (0.006 mm/hr), the reverse is nominally expected to be the case. There is sufficient uncertainty in the reaction rates on the one hand, and the potential for convective mixing on the other to render these statements highly speculative.

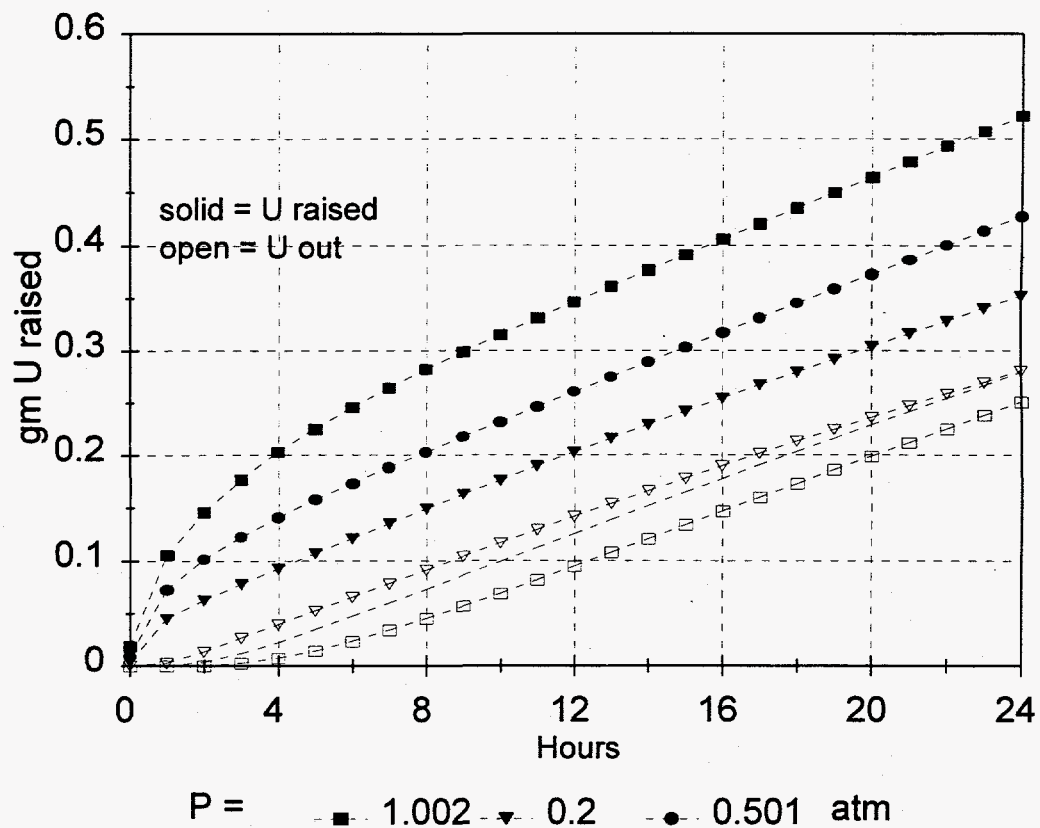
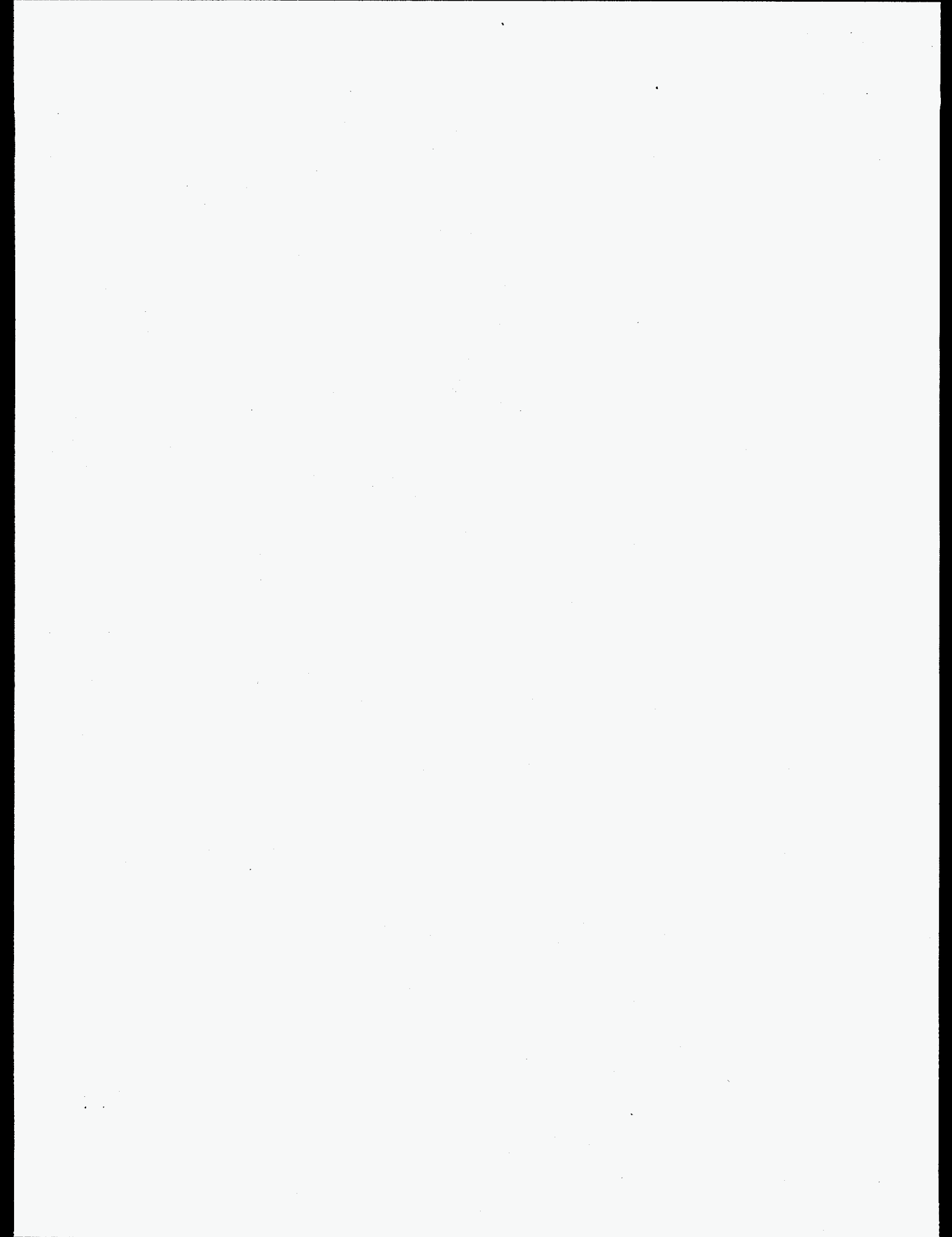


Figure B-1 Volatilization of  $UF_6$  deposit at end of a 1 meter long dead-end pipe 1  $cm^2$  cross-sectional area, modeled assuming that reaction with  $ClF_3$  is diffusion-limited. 50%  $ClF_3$ , 50% He; total pressure as indicated; "U out" refers to U (as  $UF_6$ ) diffused out the 1-meter pipe; "U up" includes, in addition,  $UF_6$  still in the pipe.

**APPENDIX C**

**AIR EMISSIONS OF Cl<sub>2</sub>**



**Air Emissions of Cl<sub>2</sub>**

Following is the text of E-mail correspondence relating to the emission of Cl<sub>2</sub> from RGRS operation. Emission of Cl<sub>2</sub> is the only significant addition to emissions from RGRS resulting from use of ClF<sub>3</sub>, as compared to emissions expected in the original RGR program. Note that the quantities and numbers of treatment batches below are intended to be overestimates and should not be used as indicating a specific plan for a treatment program.

---

Date: Thu, 09 Jan 1997 12:53:04 -0500  
To: wolfejmjr (Joseph M Wolfe)  
From: ldt@ornl.gov (Lee D. Trowbridge)  
Subject: MSRE - Potential Atmospheric Venting of Cl<sub>2</sub>  
Cc: faulknerl, hedrickcljr

## MEMO

Date: Jan 9, 1997  
To: Joe Wolfe  
Cy: R. L. Faulkner  
From: Lee Trowbridge  
Subject: MSRE Scenarios - Possible atmospheric venting of Cl<sub>2</sub>

The first several MSRE gas removal batches have revealed the existence of several plugs in the MSRE piping. These are most likely caused by deposits of solid uranium compounds - UO<sub>2</sub>F<sub>2</sub>, UF<sub>5</sub>, or UF<sub>6</sub> - which physically block flow at several separate locations. The deposits closest to the RGRS are not pure UF<sub>6</sub>, as that would sublime and lead to gas composition and pressure behavior that is not being experienced. The deposits may consist of UF<sub>5</sub> (produced by autoradiolysis of solid UF<sub>6</sub>) or UO<sub>2</sub>F<sub>2</sub> (produced by reaction with inleaking atmospheric moisture). They might also consist largely of UF<sub>6</sub> solid, but with a layer of non-volatile material which impedes evaporation of UF<sub>6</sub> when the RGR is put under vacuum.

Whatever the nature of the deposits, if they consist of solid uranium compounds as is most plausible, we need remove them, or at least break through the deposits sufficiently to adequately communicate with other areas of the MSRE piping and fuel tanks. A relatively non-intrusive way to do this is to introduce a more reactive fluorinating agent which can convert any of the non-volatile deposits to UF<sub>6</sub>. F<sub>2</sub> (already present in the MSRE system) would do this, but only if the temperature could be raised a few hundred degrees, which is, of course, not practical. A compound often used to convert non-volatile uranium deposits to UF<sub>6</sub> is ClF<sub>3</sub>. While its optimum reaction rate occurs at about 100C, the room temperature rate is still useful, being about 20% of the 100C rate for conversion of (for example) UF<sub>4</sub>. The reaction rate of ClF<sub>3</sub> with UO<sub>2</sub>F<sub>2</sub> will be slower, but still usable at room temperature.

We are at present examining the various issues related to use of ClF<sub>3</sub> in the MSRE. On one such issue, we need your advice.



The presently installed chemical trapping system consists of three traps in series containing, in order, NaF, activated alumina, and molecular sieve. The waste gas from a  $\text{ClF}_3$  treatment will contain  $\text{ClF}_3$ ,  $\text{ClF}$ ,  $\text{ClO}_2\text{F}$ , and  $\text{Cl}_2$ . The relative quantities will depend on the degree of reaction of the original  $\text{ClF}_3$ , gas mixing efficiency, and other factors. Whatever the composition, we would envision pumping the gas through the trapping system just as in the current procedure for RGR from the MSRE system.

$\text{ClF}_3$  and its reaction products will be unaffected by the NaF trap. In the activated alumina trap,  $\text{ClF}_3$  and its products will lose their fluorine, but at this point it is not clear what the fate of the chlorine will be. Thermodynamic analysis indicates that the chlorine cannot chemically be bound by the alumina as is the case with fluorine. The reaction products of the gases listed above should consist of  $\text{AlF}_3$ (solid),  $\text{Cl}_2$ , and  $\text{O}_2$ . It is possible that the very high surface area of activated alumina will physically adsorb  $\text{Cl}_2$ , but we do not know this is the case, or (if so) what the loading capacity would be. Molecular sieve is chemically and physically similar to activated alumina and the same remarks apply. Lab experiments are planned in which this series of traps will be exposed to simulated treatment gas, but we will not have the answers to these questions for a while.

For the moment, we must make the assumption that the chlorine content of the treatment gas, if passed through the existing trapping system, will emerge as  $\text{Cl}_2$ . Alternate trapping schemes or additional hardware are possible, but will cause delays and complicate later chemical processing and impose additional hardware costs. Our general question to you is: Can we vent  $\text{Cl}_2$  in the quantities which could be generated during these treatments? The following is a rough bounding scenario for the quantities that we are considering generating:

Assumptions:

1. Present flow limitations through the trapping system (1 std liter/min) will apply during removal of  $\text{ClF}_3$ -containing treatment gas. These limits are imposed to limit reactive heating in the alumina trap.
2. The treatment gas will be pumped into one holding tank (volume: 10 cu ft or 283 liters) to a pressure of 1 atmosphere prior to holding and eventually venting.
3.  $\text{ClF}_3$  is present to the extent of 30 mole % in the original treatment gas (the balance being inert gases).
4.  $\text{ClF}_3$  (or its reaction products) will react in the alumina and molecular sieve traps to produce  $\text{Cl}_2$ , which (for purposes of this analysis) is assumed NOT to be held in either trap.

Using these assumptions, we calculate the following:

- A. The gas entering the holding tank will do so at 0.85 standard liters/min (0.7 inert and 0.15 std l/m  $\text{Cl}_2$ ); the  $\text{Cl}_2$  concentration is 18 mole %.
- B. Filling a holding tank to 1 atm will take over 5 hours. Thus it is not likely that there will be more than one such batch per day, but I will assume that there are 3 holding tank volumes per day to be vented.
- C. The total quantity of gas vented will be  $3 \times 283 = 850$  std liters, of which 150 std liters will be  $\text{Cl}_2$  and 700 will be inert gases (He and  $\text{O}_2$ ). One standard liter is equivalent to 0.041 gm moles or (for  $\text{Cl}_2$ , Mol wt = 71) 2.9 gm  $\text{Cl}_2$ . The mass of 150 std liters of  $\text{Cl}_2$ , then, will be 435 gm, just under one pound.

If our assumptions are at all correct, this represents an overestimate of the upper limit to emission of  $Cl_2$ , should no additional measures be taken to capture it. Is this quantity of regulatory concern? What do we need to do to allow us to proceed along this course (that is, should the lab experiments indicate that  $Cl_2$  actually passes the alumina and molecular sieve traps)? We would appreciate your advice and any other help you can provide on this issue.

---

Date: Fri, 17 Jan 1997 17:03:21 -0500  
To: ldt@ornl.gov (Lee D. Trowbridge)  
From: wol@ornl.gov (J. M. Wolfe)  
Subject: Re: MSRE - Potential Atmospheric Venting of  $Cl_2$   
Cc: faulkner1@cosmail1.ctd.ornl.gov (Richard L Faulkner),  
skipperdd@cosmail1.ctd.ornl.gov

Lee,

I have reviewed the 1/9/97 memo describing possible  $Cl_2$  emissions from the MSRE Project. I also reviewed our 9/95 correspondence, and have determined that my 10/11/95 memo to you should be revised.

The activities you are conducting and the resulting emissions to the atmosphere do not require an air permit. This work is exempt from permitting because it is a CERCLA project. However, you would still have to meet applicable requirements and appropriate recommendations (ARARs) that would have been imposed had a permit been required. Since this source would be exempt in the absence of CERCLA, there are no ARARs.

TDEC Rule 1200-3-9-.04(5)(a)4.(i) indicates that "Any air emissions from an air emissions unit or activity at a stationary source for which the emissions unit or activity has a potential to emit less than 5 tons per year of any regulated air pollutant that is not a hazardous air pollutant, or less than 1,000 pounds per year of any hazardous air pollutant..." is an Insignificant Activity and would not require an air permit. However, "Such emission units and activities must be listed in the [Title V] permit application."

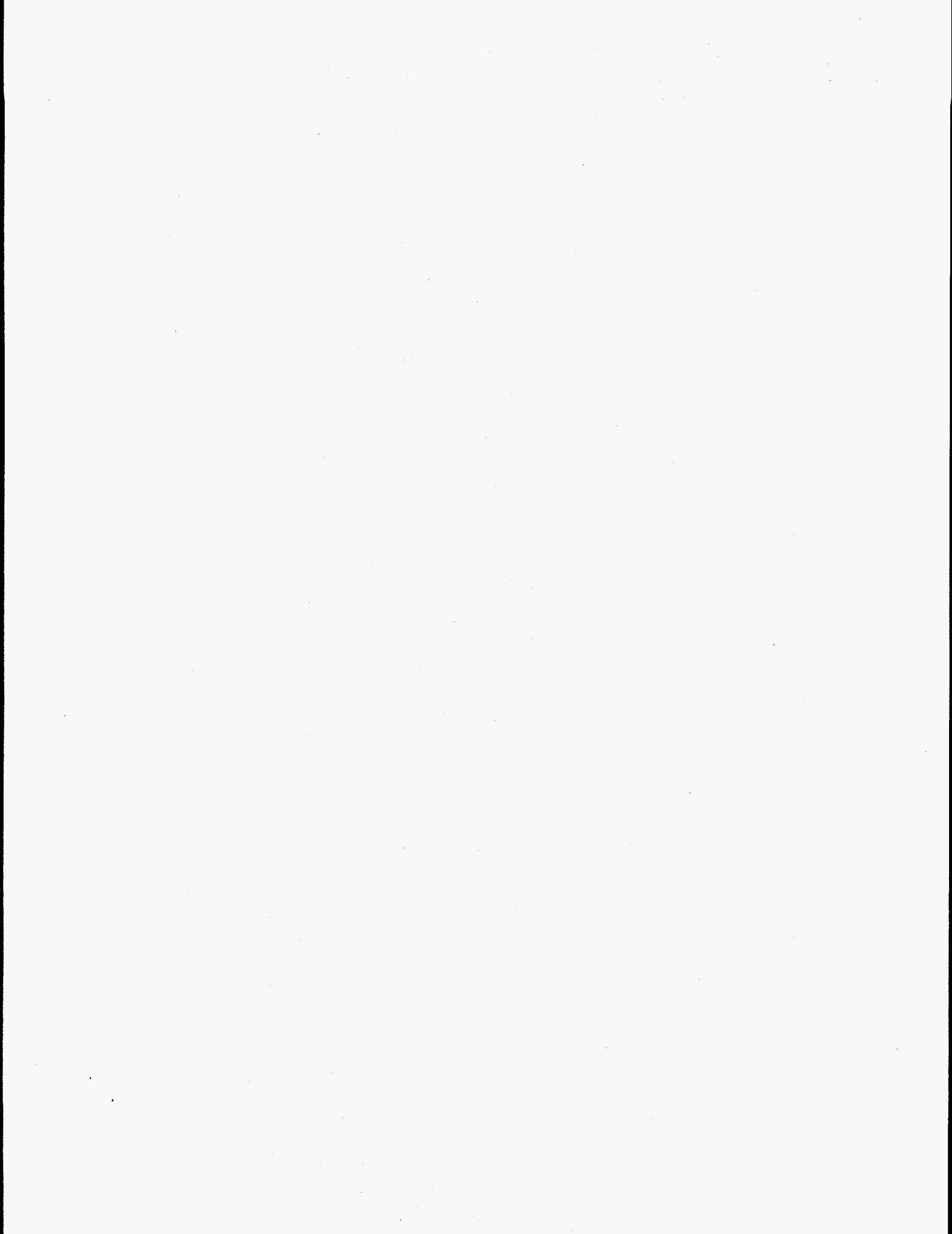
Chlorine is a Hazardous Air Pollutant, however the work referenced in your 9/25/95 correspondence, and the work described in your 1/9/97 memo would qualify as an Insignificant Activity due to the low emissions. Further, the Air Quality Compliance Team will not list this activity in the Title V permit application due to the CERCLA exemption.

Please call on me if I can assist you further.

Joe Wolfe (4-8773)

**APPENDIX D**

**MATERIALS COMPATIBILITY**



**Materials Compatibility**1. Survey of specifications valves in MSRE

Date: Mon, 21 Apr 1997 10:11:01 -0400  
To: trowbridgeld@cosmail4.ctd.ornl.gov (Lee D Trowbridge)  
From: Tom Morelock <ctm@ornl.gov>  
Subject: MSRE Valves

**Hoke TY-440 Valve**, packless, bellows sealed, maximum operating pressure 400 psig, maximum operating temperature 350 °F, minimum 0.3 Cv performance, overall maximum height 4" x 1-1/2" length face to face, stainless steel bellows assembly, replaceable teflon gaskets and seats, all wetted parts (other than disc or plug) shall be stainless steel; aluminum bonnet, end connections shall be socket weld.

( HVS-1 )

518G, 557B, 560B, 567A, 567B, 567C, 567D, 571A, 572A, 574A, 576A

**Hoke LY-473 Valve**, packless, bellows sealed, maximum operating pressure 400 psig, maximum operating temperature 350 °F, minimum 1.0 Cv performance, overall maximum height 7" x 2-3/4" length face to face, stainless steel bellows assembly, replaceable teflon gaskets and seats, all wetted parts (other than disc or plug) shall be stainless steel; aluminum bonnet, end connections shall be socket weld.

( HVS-2 )

557A, 557C, 560A,

**Hoke LY-473, Modified Valve**, packless, bellows sealed, maximum operating pressure 400 psig, maximum operating temperature 350 °F, minimum 1.0 Cv performance, overall maximum height 7" x 2-3/4" length face to face, stainless steel bellows assembly, metal to metal seats, all wetted parts (other than disc or plug) shall be stainless steel; aluminum bonnet, end connections shall be socket weld.

(HVS-2B)

518A, 518B1, 518B2, 518B3, 518C1, 518C2, 518C3, 518D, 518E, 518F, 522A, 522B,  
537, 538A, 538B, 571B,

**Hoke HY-477 Valve**, packless, bellows sealed, maximum operating pressure 2000 psig, maximum operating temperature 600 °F, minimum 1.0 Cv performance, overall maximum height 7" x 2-3/4" length face to face, connections are schedule 80, 316 stainless steel pipe welded into body, each connection extends 2 9/16", stainless steel bellows assembly welded to body, all metal construction, all wetted parts shall be stainless steel; completely welded design.

524E, 524F, 524G, 561, 620, 621, 622, 623,

**Hoke TY-445 Valve**, packless, bellows sealed, maximum operating pressure 2000 psig, maximum operating temperature 600 °F, minimum 0.3 Cv performance, overall maximum height 4" x 1-1/2" length face to face, connections are 3/8" 316 stainless steel tube 0.065 wall, stainless steel bellows

assembly welded to body, all metal construction, all wetted parts shall be stainless steel; completely welded design.

522C, 556A,

**Hoke RB271** Valve, needle, brass, size 1/4" FPT, teflon stem tip.

556B, 569A, 569C

**Hoke 4RB281** Valve, metering, brass, size 1/4" FPT,

569B

**Hoke PY271K** Valve, needle, stainless steel, Type 316, size 1/4" FPT, teflon stem tip.

**NUPRO SS-6BW-TW** All-welded construction, hermetically sealed for high temperature cycling to 900 °F, welded body-to-bellows seal, 0.39 Cv, 316 stainless steel

562C1, 562C2,

**NUPRO M-6BW-TW** All-welded construction, hermetically sealed for high temperature cycling to 900 °F, welded body-to-bellows seal .039 Cv, alloy 400

V8, V11,

**NUPRO SS-4BRW-TW** All-welded construction, for temperature to 600 °F, welded body-to-bellows seal, regulating stem insert for greater flow control, 0.26 Cv, 316 stainless steel

562B1, 562B2, 562C3

**NUPRO M-4BW-TW** All-welded construction, hermetically sealed for high temperature cycling to 900 °F, welded body-to-bellows seal .039 Cv, alloy 400

572B, 574B,

**AUTOCLAVE 30V-6001**

524C

**FULTON SYLPHON Co HRP303** 1/4" stainless steel, all metal construction, 2,000 psi  
300 °F

526, 624, 625, 626, 627, 562A,

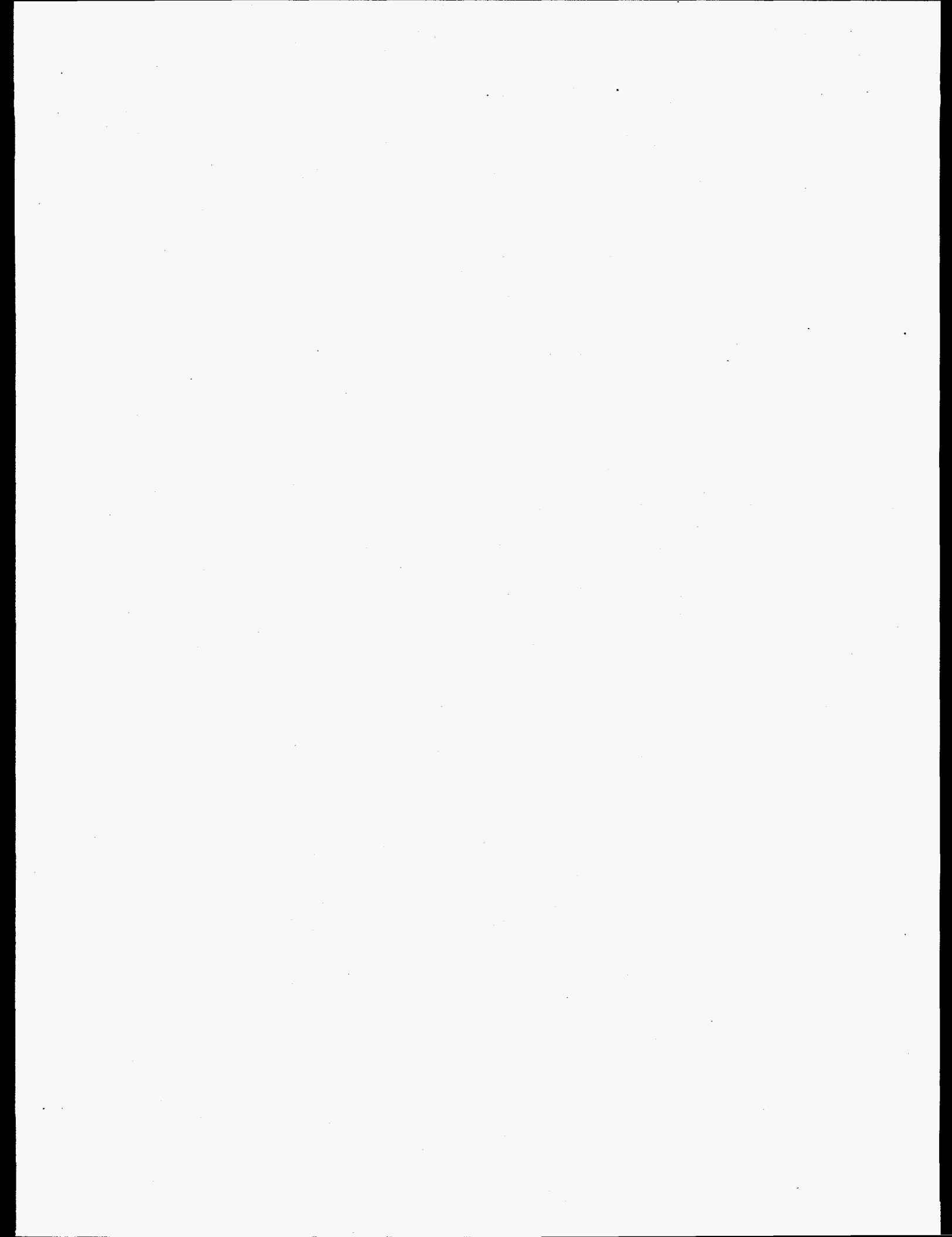
Reference Drawings: 56252, 56253, 56254, 56371, 56372, 48783, 41880, 41888, 48785, 48775,  
51519, 41495

TCM 3/21/97

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**APPENDIX E**

**CHLORINE OXIDE HAZARDS**





**Chlorine Oxide Hazards**

A letter report containing results of a literature review and evaluation of chlorine oxide hazards and recommended limits follows.

LOCKHEED MARTIN



## Memorandum

Date: March 14, 1997  
To: C. L. Hedrick  
Copy: R. L. Faulkner, L.M.Toth, D. R. Williams, J. C. Rudolph, Q. Grindstaff, N. R. Smyrl  
From: L. D. Trowbridge  
Subject: Chlorine Oxide Safety Limits in MSRE/RGR

Disposal of  $\text{ClF}_3$  and its reaction products via the existing activated alumina and molecular sieve chemical traps in the MSRE RGRS has the potential for producing chlorine oxides, which under certain conditions, can be spontaneously flammable and explosive. This letter summarizes the results of a literature search and evaluation that I undertook to enable interpretation of future operational observations in the RGRS, the ultimate intent being to assure that we avoid potentially hazardous conditions.

$\text{ClF}_3$  and its reaction products, upon reacting with activated alumina or molecular sieve, should be converted to aluminum fluoride, molecular oxygen ( $\text{O}_2$ ), and molecular chlorine ( $\text{Cl}_2$ ). These are the thermodynamically stable products in this system. If, however, the reaction does not proceed to full thermodynamic equilibrium, some of the chlorine may emerge from the trapping system as chlorine oxyfluorides or chlorine oxides.

Chlorine oxyfluorides ( $\text{ClO}_2\text{F}$  and  $\text{ClO}_3\text{F}$ ), though unstable in a thermodynamic sense, are kinetically very stable, requiring temperatures of 300 to 400°C for decomposition and having no reputation for explosive decomposition. These compounds will not be discussed further.

The most likely chlorine oxides are  $\text{Cl}_2\text{O}$  and  $\text{ClO}_2$ . Both gases are unstable to decomposition into  $\text{Cl}_2$  and  $\text{O}_2$ , and decomposition can occur spontaneously at a room temperature. Their decomposition occurs by chain reaction mechanisms. Decomposition can occur benignly or accelerate to an explosion.

The term explosion carries a slightly different meaning in the reaction rate literature from the conventional layman's definition of the term. In reaction rate literature, the term "explosion" encompasses any fairly rapid, self-propagating reaction, and includes two regimes of interest to us: "deflagration" and "detonation". A deflagration is a self-propagating reaction that proceeds through a mix of reactive material (gas in our case) at subsonic velocities, generally driven by its heat of reaction. Flame front velocities for chlorine oxides in the deflagration regime are on the order of a few meters per second. A detonation is a supersonic propagation of the flame front, generally driven by compressive heating in the shock wave. Front speeds for chlorine oxide detonations are on the order of 1000 to 1300 m/s. The detonation regime is clearly one that must be avoided; the deflagration regime is also one that we would hope to avoid, but in a contained, non-flammable apparatus able to withstand the adiabatic pressure rise of the reaction, could be tolerated. In the regime that I term "benign decomposition", decomposition occurs slowly without appreciable heating or rate acceleration; no high temperatures or pressure bursts are generated. (Note:

preliminary reports of trap testing suggests we will be well within this "benign decomposition" realm, to the extent that *any* chlorine oxides are produced at all).

Though flame and explosion reactions have been studied for over 150 years, the conditions at which explosions can occur are not terribly well-defined. Limits seem to exist for temperature, pressure, degree of dilution. The rates are affected by surface condition, volume of container, and gas activation (e.g. by addition of radicals, UV exposure, etc.). Decomposition can occur spontaneously (thermal decomposition) or can be induced externally (e.g. by a spark; visible light or UV radiation). The fact that UV radiation tends to promote initiation of decomposition suggests that nuclear radiation would do the same, though I found no direct references to such an influence.

## $\text{ClO}_2$

According to Ben Caid<sup>1</sup>, below ca. 50% concentration (in He) a detonation will not develop even for an infinite sized container; below ca. 3% or so (varying with diluent gas), the decomposition could not be made to propagate at all. Between these limits, the decomposition, once set off (by a spark, say) will propagate at subsonic velocities. The velocity of the reaction (of the flame front) is fairly slow (ca 2 to 3 m/s) up to a  $\text{ClO}_2$  mole fraction of about 50%. Other sources suggest slightly different limits or list similar limits on a different basis. Von Elbe and McHale<sup>2</sup> suggest that below about 45°C, decomposition is benign, and will not generate a flame-type reaction even if sparked. Crawford<sup>3</sup>, however, observed a course for the thermal decomposition reaction (at 24°C and above, 3.4%  $\text{ClO}_2$  in air) that matched the behavior at higher concentrations: after an induction period during which no changes were observed in the gas, the reaction rate (as determined by pressure change and spectroscopic observations) accelerated. The rate, however, was so slow (apparently taking hours to go to completion) as to not to produce any noticeable temperature rise or consequent thermal runaway at room temperature (or indeed up to about 43°C). It is not surprising that other workers, comparing such behavior to the sometimes exciting results at higher temperature would term it "unreactive".

Cowley<sup>4</sup> provides a diagram that is a synthesis of these sources, showing the pressure and temperature limits as an envelope of, in effect, benign decomposition. At 25°C, the pressure limit is about 15 Torr (ca 2% or an atmosphere, absolute or partial pressure, though there isn't detailed solid data for such an absolute pronouncement). Within these limits, even sparking didn't set off pure  $\text{ClO}_2$  or mixtures. It is not clear, however, whether it would be possible for some radical-generating mechanism (photolysis or radiolysis) to shrink these boundaries. In any case, the effect of such a reaction in a metal container should be nil at such low partial pressures.

Of more concern would be conditions in which deflagration could occur. Even if the "dark, thermal decomposition" induction time prior to autoignition were long enough for our process, there is no guarantee that our system would be either (1) free of initiating events (static discharge?) or of a foreshortening of the induction period by radiolysis. Thus, if the  $\text{ClO}_2$  concentration proves to lie within the deflagration region, we need to assure ourselves that a deflagration, if it occurred, would be contained with no adverse consequences, or that it could be avoided (e.g. by dilution).

The detonation region, in my opinion, should be avoided altogether. It appears in any case that we cannot credibly achieve such conditions if we start with a treatment gas that consists of 50% or less  $\text{ClF}_3$  diluted with He or  $\text{F}_2$ .

The practical interpretation of these observations is that, should  $\text{ClO}_2$  be produced in low concentrations and stored in the holding tank, it will decompose, possibly at an accelerating rate with time or radiation exposure.

At low concentrations, however, it is not likely that this will be noticed except by the loss of  $\text{ClO}_2$  band strength in IR spectra. Not unless concentrations reach the realm in which deflagration can occur will the decomposition take place fast enough to produce a temporary heat-of-reaction-induced pressure rise. Preliminary reports of experimental results on alumina trap behavior on exposure to  $\text{ClF}_3$ , suggest that chlorine dioxide is seen only very briefly just at trap breakthrough, and that it does not survive the molecular sieve. Even if there were no molecular sieve trap present, the quantity and concentration observed, diluted with gas already in the holding tank, cannot credibly do other than slowly and harmlessly decompose.

An oft-quoted rule-of-thumb<sup>5,6</sup> for a safe level of  $\text{ClO}_2$  in air at one atmosphere is 10%. This appears to be an empirical level taking into account the propensity for reaction and the violence (or lack thereof) should reaction occur; as such the level is situation-dependent. For purposes of MSRE/RGR, I would recommend a lower level of concern to avoid even the appearance of uncontrolled reaction.

## $\text{Cl}_2\text{O}$

$\text{Cl}_2\text{O}$  also has a reputation for being explosive, but it is much less hazardous than  $\text{ClO}_2$ . At high partial pressures, it can undergo deflagration, but from my review of the literature, it was not clear that anyone had ever induced a detonation with gaseous  $\text{Cl}_2\text{O}$  at room temperature. It is plausible that  $\text{Cl}_2\text{O}$  might form in RGR conditions. It tends to be produced under circumstances in which  $\text{Cl}_2$  is exposed to water or hydrates, (which the molecular sieve and activated alumina could be considered to be). This compound has not been positively identified in any of our experimental tests, but one reason for this may be its rather weak IR absorption spectrum.

While some researchers were unable to induce explosions (deflagrations) below about 40°C, Cady & Brown<sup>7</sup> produced deflagration (by spark) for 25-30%  $\text{Cl}_2\text{O}$  in  $\text{O}_2$  at 23°C, and stronger deflagration above 30%  $\text{Cl}_2\text{O}$ . They were unable to induce deflagration for concentrations at or below 23.2 mole %. Detonation is apparently not observed except at significantly higher initial temperatures and pressures.

There is a possibility that small amounts of  $\text{Cl}_2\text{O}$  will be produced in the RGRS, but the stoichiometry of the hypothetical reaction of (diluted)  $\text{ClF}_3$  to  $\text{Cl}_2\text{O}$  in the activated alumina trap would make it very difficult to produce  $\text{Cl}_2\text{O}$  at flammable concentrations.

## Recommendations and Conclusions

Approximate limits for concentrations of  $\text{ClO}_2$  and  $\text{Cl}_2\text{O}$  which are not flammable have been deduced from literature reports and are listed in the table below. The gas entering the holding tank should be monitored via IR during periods when  $\text{ClF}_3$  or its reaction products are passing through the chemical trap system, at least until sufficient experience is built up to indicate that this is a complete non-issue. If, based on IR measurements, it ever appears that the holding tank concentrations could be rising to the action levels, then action should be taken to stop the introduction of chlorine oxide-containing gas into the holding tank. The tank should either be diluted with purge gas (to keep the concentrations sufficiently low), or held and vented prior to introduction of more processed gas containing that level of chlorine oxides.

**Provisional Estimate of Mole Fraction limits:**(spark initiated; room temperature; ca 1 atm in O<sub>2</sub>/Cl<sub>2</sub>/He)

	Cl <sub>2</sub> O	ClO <sub>2</sub>
benign	< 23%	< 2...4 %
deflagration	23-30%+	4-50%
detonation	[A]	> 50%
"Rule-of-thumb"	<30%	<10%
safe level		
Recommended action	20%	2%
level for RGRS		

*Note [A] - No clear level for spark-initiated detonation found in literature; one reference said that below 110°C, no strong explosions occurred even for pure Cl<sub>2</sub>O; another indicated explosions strong enough to break glass container for pure, illuminated Cl<sub>2</sub>O at < 1 atm.*

Based on lab testing preliminary results reported by Williams<sup>8</sup>, it appears unlikely that these concentrations will ever be observed. In my comments on the action levels for chlorine oxides, I refer to the average concentration in the holding tank, not the momentary concentration of gas that may be measured for a short time. Williams reported seeing ClO<sub>2</sub> in measurable quantities only very briefly immediately before trap breakthrough\* (and that between the alumina and molecular sieve trap). Should a brief period of chlorine oxide evolution be experienced, it should be borne in mind that this gas will be diluted by large quantities of other gases.

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4. G. Cowley, *Loss Prevention Bulletin* **113**, Sterling Pulp Chemicals, Ltd., 2 Gibbs Rd, Toronto, Ontario, (1997)
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6. R. L. Farrar, Report K-1416, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, TN (1960).
7. G. H. Cady and R.E. Brown, *JACS* **67** p 1614 (1945).
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\* *Correction: As stated in the above memo, ClO<sub>2</sub> was observed only for a few minutes of the 3 hour trapping runs, but this occurred well in advance of ClF<sub>3</sub> breakthrough, not "immediately before" as stated in the original letter.*

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