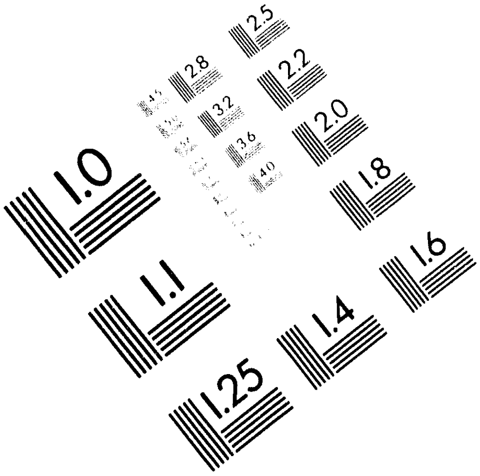

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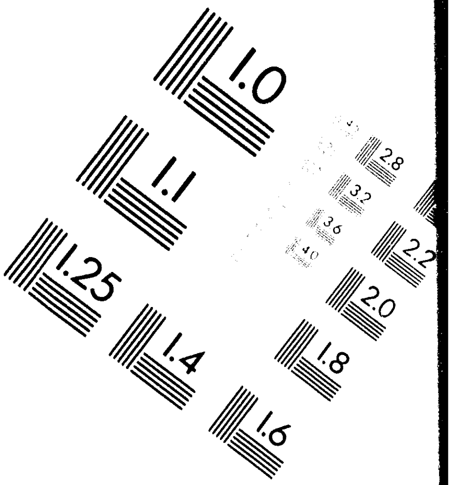

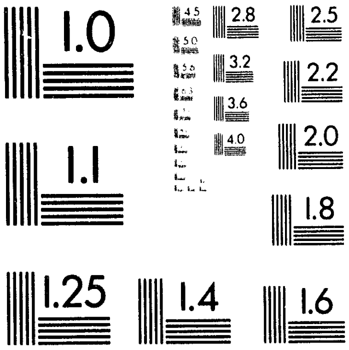

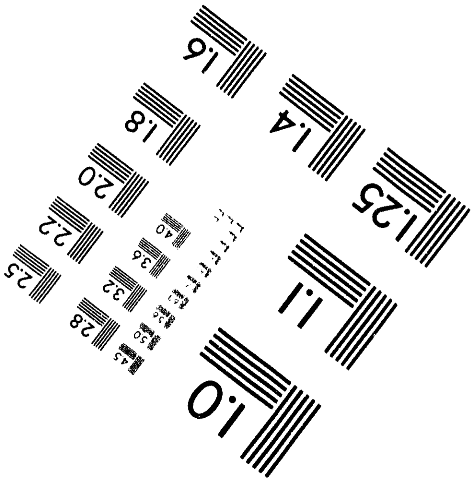

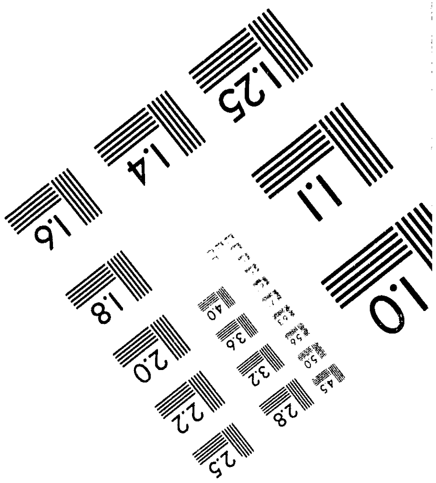

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OFF-GAS RECYCLE FOR LONG-TERM LOW TEMPERATURE GAS PHASE URANIUM DECONTAMINATION[*]

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INTRODUCTION

D&D of the process facilities at the gaseous diffusion plants (GDPs) will be an enormous task. The EBASCO estimate places the cost of D&D of the GDP at the K-25 Site at approximately $7.5 billion. Of this sum, nearly $4 billion is associated with the construction and operation of decontamination facilities and the dismantlement and transport of contaminated process equipment to these facilities (Ebasco 1991). *In situ* long-term low-temperature (LTLT) gas phase decontamination is being developed and demonstrated at the K-25 site as a technology that has the potential to substantially lower these costs while reducing criticality and safeguards concerns and worker exposure to hazardous and radioactive materials.

The objective of gas phase decontamination is to employ a gaseous reagent to fluorinate nonvolatile uranium deposits to form volatile UF_6, which can be recovered by chemical trapping or freezing (Bundy et al. 1994). The LTLT process permits the decontamination of the inside of gas-tight GDP process equipment at room temperature by substituting a long exposure to subatmospheric ClF_3 for higher reaction rates at higher temperatures. Laboratory-scale experiments have demonstrated the feasibility of using LTLT gas phase decontamination with ClF_3 to remove uranium deposits from this equipment (Munday and Simmons 1993). A mobile gas phase system is being designed to demonstrate the decontamination process on a full scale (Munday 1993; Theta 1993). If used to decontaminate the GDPs, the LTLT process would use large amounts of ClF_3 and exhaust large volumes of by-product gases (ClF, ClO_2F, etc.). Initially, the excess ClF_3 and reaction by-products will be destroyed in a KOH scrubber. This paper describes a proposed system that could recover the excess ClF_3 and regenerate the reaction by-products into ClF_3 for use in decontamination of additional equipment. Use of this regeneration and recovery system would reduce raw material costs and also reduce the waste scrubber sludge disposal costs by reducing the amount of corrosive gases fed to the scrubber.

CONCEPT

The regeneration system would thermally decompose ClO_2F into ClF and O_2; react ClF with F_2 in the presence of a heated nickel catalyst to form ClF_3; and recover ClF_3 from the mixture of gases leaving the reactor by cold trapping. The expected reactions are:

$$ClO_2F \rightarrow ClF + O_2$$

for the thermal decomposition of ClO_2F and

$$ClF + F_2 \rightarrow ClF_3$$

for the regeneration of ClF_3.

Figure 1 is a schematic diagram of the regeneration system. Spent gases from the gas phase decontamination process will be brought to the regeneration system in a portable tank. All but trace amounts of the UF_6 and HF (from the reaction of ClF_3 with the waters of hydration associated with UO_2F_2) formed during the LTLT gas phase decontamination reactions will have been removed from the spent process gas by NaF chemical traps before

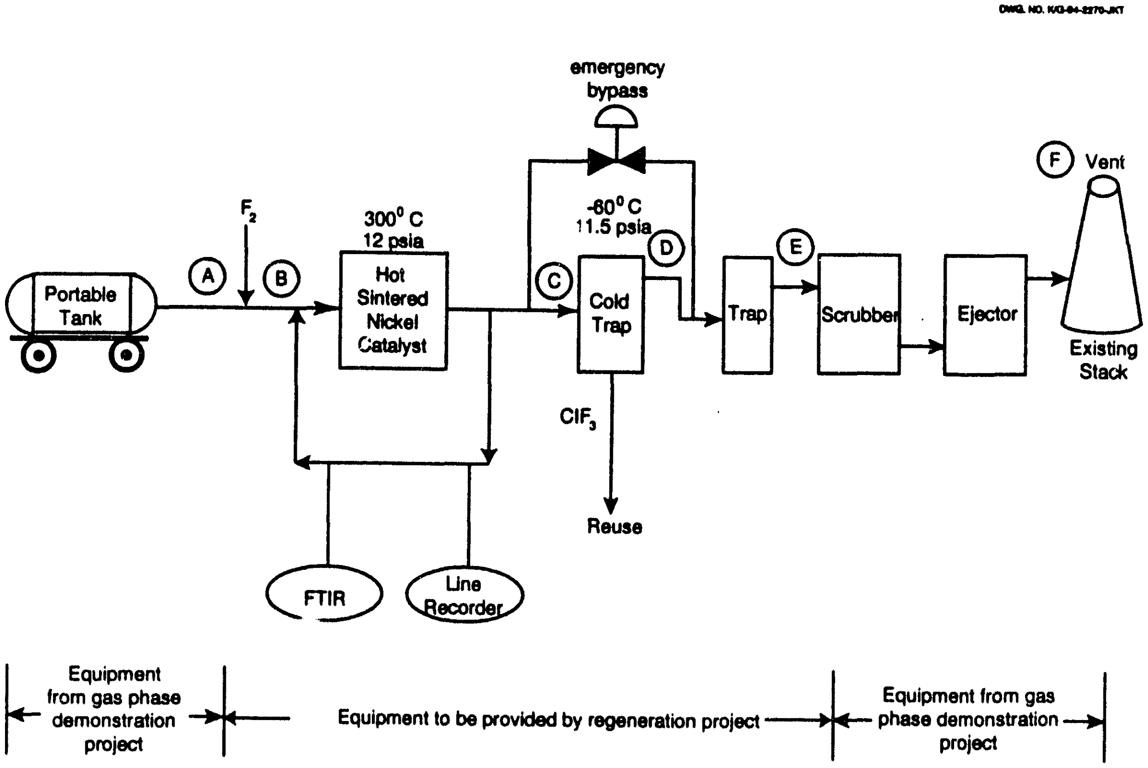

Figure 1. Schematic Diagram of ClF_3 Regeneration System

these gases are released into the portable tank. The feed gases will be mixed with F_2 and passed through a plug flow reactor packed with nickel catalyst pellets at an elevated temperature. A recycle loop around the reactor will be used to obtain the desired yield. The system will be operated below atmospheric pressure to prevent the loss of reactive gases into the building.

A Fourier transform infrared spectrometer (FTIR) will monitor the reactor products to be sure that ClO_2 is not present in the product gases before these gases enter the cold trap that follows the reactor. The cold trap will be by-passed if ClO_2 is detected. These precautions are needed to assure that ClO_2 is not condensed because ClO_2 may detonate as it evaporates. Chlorine dioxide is not a stable product of the thermal decomposition of ClO_2F in the presence of F_2. A mass spectrometer will be used to monitor the gases exiting the reactor to assure that an excess of F_2 is always present.

If ClO_2 is not detected by the FTIR, the product gases will then pass through a cold trap, where ClF_3 will be condensed. The remaining gases will pass though the off-gas treatment system, which will consist of an adsorbent-filled chemical trap followed by an aqueous KOH scrubber. The remaining gases will be vented through a stack.

MATERIAL BALANCES

The material balances are based on processing the spent gases from a typical decontamination process over a 6-hour period. The spent gases are assumed to result from decontamination of gaseous diffusion equipment having a volume of 1300 ft^3 using an initial charge of 4 psia ClF_3. Sufficient dry air would have been added to increase the pressure in the tank to 12 psia. The first column in Table 1 gives the composition of the gases entering the regeneration system from the portable tank (point A in Figure 1) subject to the assumptions that 1) 98% of the UF_6 is removed in the initial, hot NaF traps, 2) 99.8% of the remaining UF_6 is removed in the subsequent cold NaF traps, 3) no HF is removed in the hot NaF traps, and 4) 99% of the HF is removed in the cold NaF traps. The preliminary design assumes that 100% excess F_2 is added before the reactor. The composition of the

Table 1. Material balance for the ClF_3 regeneration system gas flow rate, lb-moles/hour

	Spent Gases	Reactor Entrance	Reactor Exit	Cold Trap Exit	Chemical Trap Exit	Scrubber Exit
LOCATION	A	B	C	D	E	F
ClF_3	0.103	0.103	0.130	0.0068	0.00034	$1.7 \cdot 10^{-5}$
UF_6	$6.1 \cdot 10^{-7}$	$6.1 \cdot 10^{-7}$	$6.1 \cdot 10^{-7}$	$3 \cdot 10^{-11}$	$3 \cdot 10^{-11}$	$3 \cdot 10^{-11}$
ClO_2F	0.0232	0.0232	0.0046	0.00078	$3.9 \cdot 10^{-5}$	$3.9 \cdot 10^{-5}$
ClF	0.0233	0.0233	0.0116	0.0116	0.00060	$3.0 \cdot 10^{-5}$
HF	0.00031	0.00031	0.00031	$2.6 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$
CO_2[1]	0.00011	0.00011	0.00011	0.00011	0.00011	$5.3 \cdot 10^{-6}$
O_2	0.0568	0.0568	0.0754	0.0754	0.0754	0.0754
N_2	0.244	0.244	0.244	0.244	0.244	0.244
F_2	0	0.093	0.0627	0.0627	0.0031	0.00016
Cl_2	0	0	0	0	0.0093	0.00046
Total	0.450	0.544	0.529	0.401	0.333	0.319

[1] Air contains 350 ppm CO_2.

gases entering the regeneration reactor (point B in Figure 1) are given in the second column in Table 1. Eighty percent of the ClO_2F was assumed to be thermally decomposed to ClF and O_2. Also, 80% of the equilibrium yield of ClF_3 at 300°C was assumed to be achieved in the reactor. Subject to these assumptions, the flow rates of the gases leaving the reactor are given in column C of Table 1.

Computations determined that virtually all of the ClF_3 product could be recovered in a cold trap operating at a temperature of -60°C. The composition of the gases leaving the cold trap operating at this temperature are given in column D of Table 1.

The adsorbent trap is assumed to remove 95% of the fluorine compounds entering the trap. The chlorine atoms in the fluorine compounds are assumed to be converted to chlorine molecules. The flow rates of the gases leaving the adsorbent trap are shown in column E of Table 1. An aqueous KOH scrubber will be used to reduce the amount of Cl_2 that is released to a level that will satisfy regulatory requirements. Past experience with KOH scrubbers at the K-25 Site indicates removal rates of at least 95% for fluorine compounds and Cl_2 (and CO_2). The gas composition that can be expected at the scrubber exit and, thus, will be vented to the environment are listed in the final column of Table 1 based upon the assumption that 95% of these materials are removed by the scrubber. It is assumed that none of the gases that already have extremely low partial pressures will be removed in the scrubber.

EQUILIBRIUM CALCULATIONS

In the absence of equilibrium data, 80% of the ClO_2F entering the reactor was assumed to be converted to ClF. The equilibrium data of Schmitz and Schumacher (1947) for the reaction:

$$ClF_3 \rightarrow ClF + F_2$$

can be summarized by the equation:

$$\log_{10}(K_p) = 7.111 - 5574/T,$$

over the range of 110°C to 350°C,

where

$$K_p = (P_{ClF} \bullet P_{F_2})/P_{ClF_3}$$

and T is the temperature in degrees Kelvin.

If the reactor operates at 12 psia, the pressure drop through the reactor is negligible, and the inlet concentrations are those given in column B of Table 1, the production of ClF_3 achieved at equilibrium will be that given in Table 2.

Table 2. Flow rates of ClF_3 achieved at equilibrium

Temperature, °C	ClF_3, lb-mole/hour
120	0.145
160	0.145
200	0.145
240	0.145
260	0.144
280	0.143
300	0.141
320	0.137
340	0.131

REACTION KINETICS

Published values (Heras, et al., 1959) for the reaction rate constant for the decomposition of ClO_2F cover a temperature range from 310°C to 340°C. Reaction rates at 310°C vary from about 0.2 to $1.3 \bullet 10^{-2}$ min^{-1}. Additional data over a wider temperature range may be needed to evaluate the proposed regeneration of ClF_3.

The kinetics data of Reiner, et al. (1994) for the reaction between ClF and F_2 can be represented (Trowbridge 1994) by the equation:

$$\frac{dn_{ClF_3}}{dt} = 2.853 \cdot 10^{-8} \cdot S \cdot P_{F_2} \cdot P_{ClF} \cdot (1 - \theta) \cdot e^{\frac{11665}{RT}} ,$$

where

dn_{ClF}/dt = rate of formation of ClF_3, moles/sec,

S = surface area of catalyst, cm^2,

P_{F_2} and P_{ClF} = partial pressure of F_2, and ClF, torr,

θ = fraction of the catalyst surface that is inhibited,

R = gas constant, 1.987 cal/mole°K, and

T = reactor temperature, °K.

During their experiments, Reiner and Simmons observed that with high concentrations of ClF_3 or UF_6 in the reactor, as much as 84% of the catalyst surface area was poisoned, or inhibited, and became inactive. They did not investigate the effects of the other by-product gases from the gas phase decontamination process. A study of the effects of these gases should be made before the final design of the ClF_3 regeneration equipment. Reactor sizing calculations were not attempted because of uncertainties in the amount of catalyst surface that would be active and the effects of other gases that would be present. Instead, the reactor was assumed to be large enough that the reaction between ClF and F_2 would reach 80% of the yield at equilibrium.

COST SAVINGS

The cost savings for the regeneration of ClF_3 would result from reduced purchases of ClF_3 and from lower costs for disposal of fluorinating gases in a scrubber. The regeneration system would recover 68.2 lb ClF_3 for each 1300-ft^3 batch of off-gases from the decontamination process. At a cost of \$23.76/lb ClF_3, this cost savings would be about \$1620/batch. The regeneration system would also reduce the amounts of corrosive gases that would react with KOH in the scrubber. The flow rates of gases entering the scrubber are shown in Table 3 to be 0.137 lb-mole/hr (0.819 lb-mole/batch) less with a regeneration system than without one. According to Munday (1993), the cost to dispose of ClF_3 in a KOH scrubber is \$12.18/lb ClF_3, which is \$1,130/lb-mole of gas treated, including disposal of the sludge generated in treating the spent scrubber solution. Thus, \$925 would be saved because of the reduction in the amount of corrosive gases that would have to be treated in the scrubber. The total saving from reduced purchases of ClF_3 and corrosive gas treatment would be \$2550/batch. Since over 3 million ft^3 of equipment may have to be decontaminated by the LTLT process, this value corresponds to a very attractive potential savings.

Table 3. Flow rates of gases entering the scrubber

Gas	Without Regeneration lb-mole/hour	With Regeneration lb-mole/hour
Cl_2	0	0.00926
ClF_3	0.103	$3.4 \cdot 10^{-4}$
ClF	0.0233	$6.0 \cdot 10^{-4}$
ClO_2F	0.0232	$3.9 \cdot 10^{-5}$
F_2	0	0.00314
CO_2	$1.1 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$
Total	0.150	0.0135

CONCLUSIONS

Regeneration and recycle of ClF_3 from the spent reaction gases from the LTLT gas phase decontamination of gaseous diffusion process equipment is economically attractive and can be accomplished using the process described in this paper. The reactor products must be monitored to assure that no ClO_2 is condensed in the cold trap. A scrubber will be needed to meet the regulatory limits on chlorine emissions. Although sufficient equilibrium and kinetic data are available to provide a basis for the proposed process, laboratory- and pilot-scale experiments are needed to establish more precisely the by-products from the gas phase decontamination reaction, determine reaction kinetics, and demonstrate safe and effective operation of the system.

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