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Investigation of Gas-Phase Decontamination
of Internally Radioactively Contaminated
Gaseous Diffusion Process Equipment and Piping

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MASTER

INTRODUCTION

Construction of the gaseous diffusion plants (GDPs) was begun during World War II to produce enriched uranium for defense purposes. These plants, which utilized UF_6 gas, were used primarily for this purpose through 1964. From 1959 through 1968, production shifted primarily to uranium enrichment to supply the nuclear power industry. Additional UF_6 -handling facilities were built in feed and fuel-processing plants associated with the uranium enrichment process.

Two of the five process buildings at Oak Ridge were shut down in 1964. Uranium enrichment activities at Oak Ridge were discontinued altogether in 1985. In 1987, the Department of Energy (DOE) decided to proceed with a permanent shutdown of the Oak Ridge Gaseous Diffusion Plant (ORGDG). DOE intends to begin decommissioning and decontamination (D&D) of ORGDG early in the next century. The remaining two GDPs are expected to be shut down during the next 10 to 40 years and will also require D&D, as will the other UF_6 -handling facilities.

This paper presents an investigation of gas-phase decontamination of internally radioactively contaminated gaseous diffusion process equipment and piping using powerful fluorinating reagents that convert nonvolatile uranium compounds to volatile UF_6 . These reagents include ClF_3 , F_2 , and other compounds. The scope of D&D at the GDPs, previous work of gas-phase decontamination, four concepts for using gas-phase decontamination, plans for further study of gas-phase decontamination, and the current status of this work are discussed.

SCOPE OF D&D AT GDPs

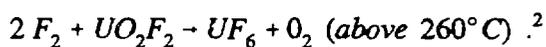
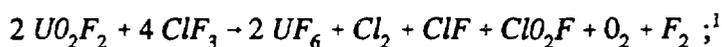
D&D of the process facilities at the GDPs will be an enormous task. ORGDG contains over 5000 stages in five process buildings, which are identified in Figure 1. A typical stage arrangement utilizing axial compressors is shown in Figure 2. Each stage consists of a converter, which contains the barrier that accomplishes the enrichment; a heat exchanger; an axial compressor; a control valve; and associated piping. Much of the equipment is quite large, as can be seen in Figures 3 and 4, which show the largest size of converter and compressor that was used. A different type of stage, which is found in two of the process buildings, is shown in Figure 5. This type of stage utilizes two centrifugal compressors per stage and contains smaller equipment than the stages that use axial compressors.

The process equipment is primarily contaminated with UO_2F_2 , which results from reaction of UF_6 with moisture leakage, and UF_4 , which is the ultimate stable product resulting from the reaction of UF_6 with the metal surfaces of the process equipment. The inside of some of the process equipment is also contaminated with technetium and, perhaps, trace amounts of plutonium, neptunium, and americium.

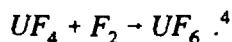
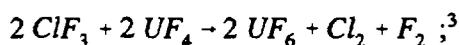
Decontamination of the process equipment and disposition of the decontaminated equipment plus the secondary waste generated by the decontamination process will be the largest task in D&D of the GDPs. However, the process buildings also contain auxiliary equipment (transformers, lube oil systems, etc.) that will require D&D as will the process buildings themselves and approximately 50 auxiliary buildings (barrier plant, cascade pilot plant, etc.) with the equipment in them. Gas-phase treatment is unlikely to be applicable to decontamination of much of the auxiliary buildings and equipment.

GENERAL CONCEPT

The objective of gas-phase decontamination treatment 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. Although there is some uncertainty about the reaction equations, the following reactions with UO_2F_2 can be written with a fair degree of confidence:



The reactions with UF_4 are generally taken to be:



This concept is illustrated very simply in Figure 6. The contaminated equipment is treated with the fluorinating gas and decontaminated. The off-gas goes to a chemical trap (or cold trap), which sorbs (or freezes out) the UF_6 . The remaining off-gas passes through a scrubber, which removes remaining fluorides, and is exhausted up a stack. The UF_6 is desorbed from the chemical trap, which regenerates the trapping material for reuse (or vaporized by heating the cold trap), and recovered in a refrigerated cylinder.

Advantages

Gas-phase decontamination has several advantages. The uranium can be recovered as UF_6 and fed into an operating GDP rather than disposed of as waste. Worker exposure to radioactivity and hazardous materials is minimized since the process is totally contained in gas tight equipment. Criticality concerns are reduced because no liquids are used and disturbance of uranium deposits is minimal. Safeguards concerns are also minimized since the uranium remains in sealed equipment and is not readily accessible to workers and others who might divert it. Cost savings from gas-phase decontamination can be substantial if the decontamination can be done *in-situ*, or if the equipment does

not have to be disassembled subsequently. Even if this is necessary, reduced security, worker protection, and contamination containment requirements can result in significant savings.

Disadvantages and Limitations

Gas-phase decontamination also has some disadvantages and limitations. Disadvantages include safety concerns with the use of highly corrosive gases, sampling and permitting requirements for gas discharges, and uncertainty in the amount of uranium that will be recovered. Earlier studies discussed in the next section obtained uranium recoveries from 70 to 98% of the uranium originally present.

Gas-phase decontamination is not applicable to all situations. Gas-phase decontamination is most applicable to treating the inside of gas-tight equipment. Gas-phase decontamination would be difficult to apply to equipment that is sufficiently plugged that a flow path through the equipment does not exist or in portions of equipment that are dead-ended relative to the flow path through the equipment since diffusion of the reagent to the deposit and diffusion of UF_6 and other reaction products away from the deposits will be slow.

Gas-phase decontamination will only be successful for contaminants that form volatile fluorides. Uranium falls into this category. However, thorium, plutonium, neptunium, and americium form nonvolatile fluorides. The fluoride chemistry of technetium is very complex, but technetium contamination is expected to be difficult to remove.

SUMMARY OF PREVIOUS WORK

F_2 , ClF_3 , and BrF_3 have been evaluated by previous investigators at U.S. DOE GDPs as agents for the decontamination of uranium deposits. Although these studies are incomplete and do not agree as to the effectiveness of gas phase decontamination, the evaluations were conducted on both a laboratory-scale and production-scale. F_2 was found to be ineffective at temperatures below $150^\circ C$, but the reactivity increased rapidly above this temperature as shown by Figure 7. Previous studies were limited to temperatures below about $200^\circ C$, but the data in Figure 7 suggest that gas phase decontamination may be much more effective at still higher temperatures.⁵ This figure is based upon data obtained during production-scale decontamination of a converter with 20% F_2 in N_2 at a total pressure of about 6 psia. BrF_3 was found to be more reactive than ClF_3 , but its use was abandoned in favor of ClF_3 because removing the low vapor pressure Br by-products from the process equipment proved difficult. Also, the by-products posed greater explosion hazards than those associated with ClF_3 . Therefore, previous decontamination studies centered around the use of ClF_3 , which is vastly more reactive than F_2 below $200^\circ C$ and will slowly fluorinate uranium contaminates at temperatures less than $23^\circ C$.

A long-term study showed that the reactivity of UF_4 deposits with ClF_3 decreases by a factor of 10 over 1 to 2 years, possibly due to slow hydration or a decrease in the surface area of the deposit. The results of a short-term laboratory study⁶ on the effects of aging UO_2F_2 samples prior to reaction with ClF_3 is shown in Figure 8. This figure indicates that reactivity decreases logarithmically with sample age.

Kinetics studies of the fluorination of UF_4 by ClF_3 conducted for the United Kingdom Atomic Energy Authority indicate that the reaction rate passes through a maximum at $105^\circ C$, falls to a minimum at $148^\circ C$, and then rises again. Possible explanations are given⁷ for the unusual departure from the Arrhenius rate equation. Other experimenters observed a similar maximum value in reactivity with temperature except the maximum was reported⁸ at $113^\circ C$ instead of $105^\circ C$.

Studies of the temperature dependence of the $UO_2F_2 - ClF_3$ reaction have given conflicting results. Figure 9 indicates a steady rise in reaction rate with temperature for different pressures and concentrations of ClF_3 .⁹ Figure 10 indicates that the reactivity decreases with temperature over the interval 103 to $138^\circ C$.⁶ The composition of the gas used in the study from which Figure 10 was taken consisted of the following partial pressures: ClF_3 (0.15 psia), F_2 (0.07 psia), and N_2 (1 psia).

Several studies show that the rate of the $UO_2F_2 - ClF_3$ reaction increases with the partial pressure of ClF_3 at various temperatures and with different diluent gases. Figure 11 indicates the rate of the $UO_2F_2 - ClF_3$ reaction for pure ClF_3 at different temperatures and for a nitrogen - ClF_3 mixture as the pressure of ClF_3 varies from 0.02 to 1.0 psia.⁹ Further studies^{10,11} indicate that the reaction rate continues to increase as the ClF_3 pressure increases towards 1 atm. Also, F_2 as well as nitrogen tend to suppress the reaction rate when used as a diluent for the ClF_3 (at least at the temperatures evaluated).

In addition to laboratory studies, full-size decontamination studies have been performed in decontamination ovens. Figure 12 shows the uranium recovery from a converter when five charges of ClF_3 were applied to the process loop (a description of a decontamination oven is given later).¹² The uranium recovery was determined from gas samples, and the off-gases were evacuated before the next charge of ClF_3 was applied. Steps can clearly be seen in the curve due to the depletion of ClF_3 , and the addition of the fresh charge. The form of the curve is typical for oven decontamination, but the process time shown in Figure 12 is unusually long, and the ClF_3 charges are unusually small. Table I shows data from the decontamination of several converters.

The decontamination results vary considerably with different studies, and the results shown in Table I are not necessarily typical. Thus, additional work is needed to definitively establish the effectiveness of gas-phase decontamination. The average alpha wipe count shown for item 3 varied from 100 to 2,200 depending on location. Note that the large majority of uranium deposits are recovered early in the process.

TABLE I. Results of gas-phase decontamination of selected converters

Ref.	Run No.	Time of run (h)	Temp. (°C)	ClF ₃ (kg)	U recovered (kg)	U remaining (kg)	Average alpha wipe reading (dpm/100 cm ²)
12	1	4.4	80	1.4	0.17		
	2	5.0	87	1.4	0.03	0.02	<200
12	1	3.7	82	1.4	0.13		
	2	3.7	79	0.8	0.00	0.04	<400
13	1	24.0	46	4.9	1.22		
	2	24.0	104	2.3	0.04		
	3	24.0	190	2.7	0.01		<800

CONCEPTS FOR GAS PHASE DECONTAMINATION

Decontamination in a Large Oven

The item requiring decontamination is installed in a large oven that will allow heating to increase the reactivity of the fluorinating gas. The process inlet and outlet of the item is sealed between a closed loop system that passes through the oven walls. The fluorinating gas circulates around the loop and through the item by means of a compressor located outside the oven. The fluorinating gas is confined at subatmospheric pressure to insure that it does not escape from the loop. Uranium recovery equipment, a roughing pump for initial evacuation of air, gas scrubbers, and other auxiliary equipment are also used. A schematic of the oven decontamination equipment is shown in Figure 13.

Following installation, the item and process loop are evacuated, leak tested, heated, and purged with dry nitrogen. F₂ is then added at an oven temperature less than 100°C and purged to remove moisture or organic residues. The desired fluorinating gas (F₂ or ClF₃) is then charged, and the oven temperature increased to operating temperature. The excess fluorinating gas, gaseous by-products, and generated UF₆ are evacuated from the loop at the conclusion of the process, and UF₆ is recovered by chemical trapping or freezing.

In-Situ Decontamination of Portions of the Cascade

The equipment requiring decontamination is modified and renovated such that the process compressors and piping form the decontamination process loop with the converters still installed in their original positions. Process heating is supplied by the heat of compression of the compressors that force the gas around the loop. The auxiliary equipment needed to charge and evacuate the gases and collect the UF_6 is installed on a trailer. The process steps and auxiliary equipment is basically the same as is used in oven decontamination. This process will allow *in-situ* decontamination of several stages of gaseous diffusion equipment at once, but will not allow operating temperatures as high as an oven.

Mobile System for Decontamination

The mobile system equipment and operation is similar to that used with the oven system. The mobile system is mounted on a trailer and is intended for *in-situ* decontamination of items located in sections of the cascade that are not in good enough condition to allow decontamination by operating a portion of the cascade. A schematic of the equipment layout on a trailer is shown in Figure 14. A compressor is mounted on the trailer to force the gas around the process loop, and heating elements are supplied to heat the gas as it flows toward the item requiring decontamination.

Long-Term Low Temperature System

Experimental data indicates that uranium deposits can be fluorinated using ClF_3 at temperatures as low as $21^\circ C$. The long-term low temperature system operation can be outlined as follows: seal the item requiring decontamination, purge with dry nitrogen, evacuate the nitrogen with a roughing pump, charge with ClF_3 to subatmospheric pressure, leave the item with the sealed charge while proceeding to process other items, then return to evacuate the UF_6 and other gases after an extended period of time (possibly months). The only equipment required is that associated with evacuating, charging ClF_3 , and collecting the off-gases. An extended time period is necessary to compensate for the slow reaction rate at low temperature.

PROGRAM PLANS AND STATUS

The investigation of gas-phase decontamination will include both laboratory studies and full-scale demonstrations.

Laboratory Studies

Need. In spite of the previous studies of gas-phase decontamination that have been discussed, further laboratory studies are required to evaluate the method's effectiveness at various operating conditions with different fluorinating reagents including ClF_3 , F_2 , and IF_7 . Laboratory-scale testing of gas-phase decontamination will be conducted in two

phases. Phase I will concentrate on producing data at conditions suitable for use in an oven to demonstrate the feasibility of this process in the shortest possible time. An urgent need exists to remove uranium deposits from some process equipment by this method. Phase II will allow development and evaluation of operating conditions for various fluorinating reagents and decontamination options.

Test Loop. The laboratory test loop is shown in Figure 15. The reactor will be a nickel pipe, 90 cm long with a 5 cm inside diameter. The reactor will be mounted in a muffle furnace with an isothermal zone 50 cm long, which can be maintained within 1°C between 50 and 500°C. A radially centered nickel thermocouple well will extend through the length of the reactor for use in monitoring the temperature. A metal-bellows gas pump will circulate the gas to the reactor. A mechanical pump protected by a chemical trap containing a mixture of soda lime and activated alumina will be used to evacuate the reactor. The loop will be constructed mainly of nickel and monel with valve packings of teflon and copper instrument lines. A nickel tube (0.3 cm diam) will extend into the center of the reactor to allow moist air to be released in the presence of UF_6 to form UO_2F_2 *in situ* on selected items, which will later serve as samples for decontamination. The system will be wrapped with heating tape energized by a variable power transformer as necessary to prevent cold spots where UF_6 would freeze out.

A fourier transform infrared spectrophotometer will measure the partial pressures of UF_6 , ClF_3 , and IF_7 . Gas pressures in the reactor and spectrophotometer cell will be measured using capacitance manometers, and a mass flowmeter will measure gas circulation rates.

Low Temperature Reactors. The long-term low temperature process will be evaluated using simple reactors made from a 3-in.-diam, 15-in. long section of nickel or monel pipe with a plate welded on one end and a flange fitting on the other end. The welded end will have a pressure indicator. Both ends will be equipped with a valve to allow evacuation and charging of gas. A pressure relief valve will also be installed. The reactors will be stored under a fume hood when containing fluorinating gas.

Planning. Initial planning for laboratory studies concerning equipment design, safety, environmental issues, procedures, and quality assurance began in FY 1990. The laboratory-scale test loop will be completed this fiscal year. Phase I laboratory studies should be completed by the end of FY 1991. Phase II test loop studies and the long-term room temperature laboratory studies are tentatively scheduled for FY 1992.

Funding was received in July 1990 to begin planning the laboratory-scale studies. Funding was received from another source in February 1991 to construct the laboratory test loop and conduct Phase I laboratory studies. Funding is being sought to complete Phase II of the laboratory studies in FY 1992.

Full-Scale Demonstrations

Depending upon the laboratory results, evaluations of three options (large oven treatments, long-term low temperature process, and *in-situ* treatments of portions of the cascade) are planned using actual contaminated process equipment. If all three processes were to be demonstrated on a full scale, the large oven demonstration might begin in FY 1992, the long-term low temperature decontamination demonstration might begin in FY 1993, and the *in-situ* treatment of entire sections of the gaseous diffusion cascade might begin in FY 1994. Each full-scale demonstration would likely require two to three years to complete. Funding has been received to develop a cost estimate for the full-scale demonstration of uranium deposit removal in a large oven.

CONCLUSIONS

Gas-phase decontamination of the tremendous amount of process equipment in the three GDPs and other UF_6 -handling facilities by fluorination of nonvolatile uranium contamination deposits to volatile UF_6 is an innovative method for decontaminating this equipment that has several potential advantages. Among these are reduced criticality and safeguard concerns, less worker exposure to radioactive and hazardous materials, possible *in-situ* treatment, and potentially large cost savings. Generally this technique is limited to decontamination of the interior of gas-tight equipment that is contaminated with materials, like uranium, that form volatile fluorides. Previous investigations of this technique are incomplete and do not agree as to its effectiveness. However, previous work provides good reason to expect that this technique will be substantially effective, particularly if the treatments involve fluorine at higher temperatures than previously used or if equipment is treated for very long times even at room temperature. Gas-phase treatments might take three forms: high temperature treatments in a stationary or mobile oven, long-term low temperature *in-situ* treatments, or *in-situ* treatments of several stages of equipment at once using a circulating gas. An experimental program has been proposed to demonstrate the effectiveness of gas-phase decontamination, first on a laboratory-scale, and then on actual full-size equipment. This program is in a very early stage of execution.

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FIGURE 1 Aerial view of Oak Ridge gaseous diffusion plant (K-25 Site).



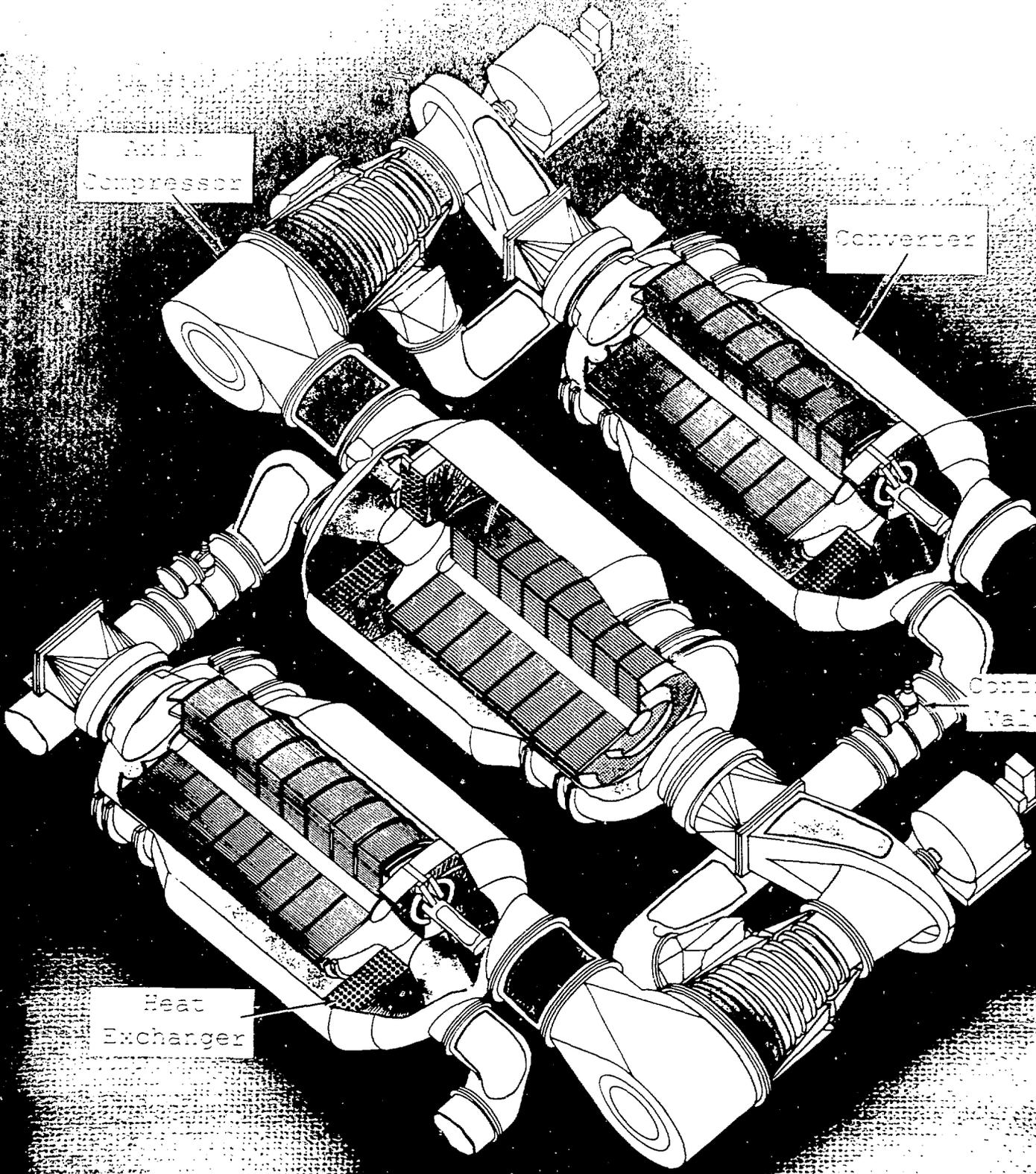
FIGURE 2 Typical U.S. gaseous diffusion stage arrangement.

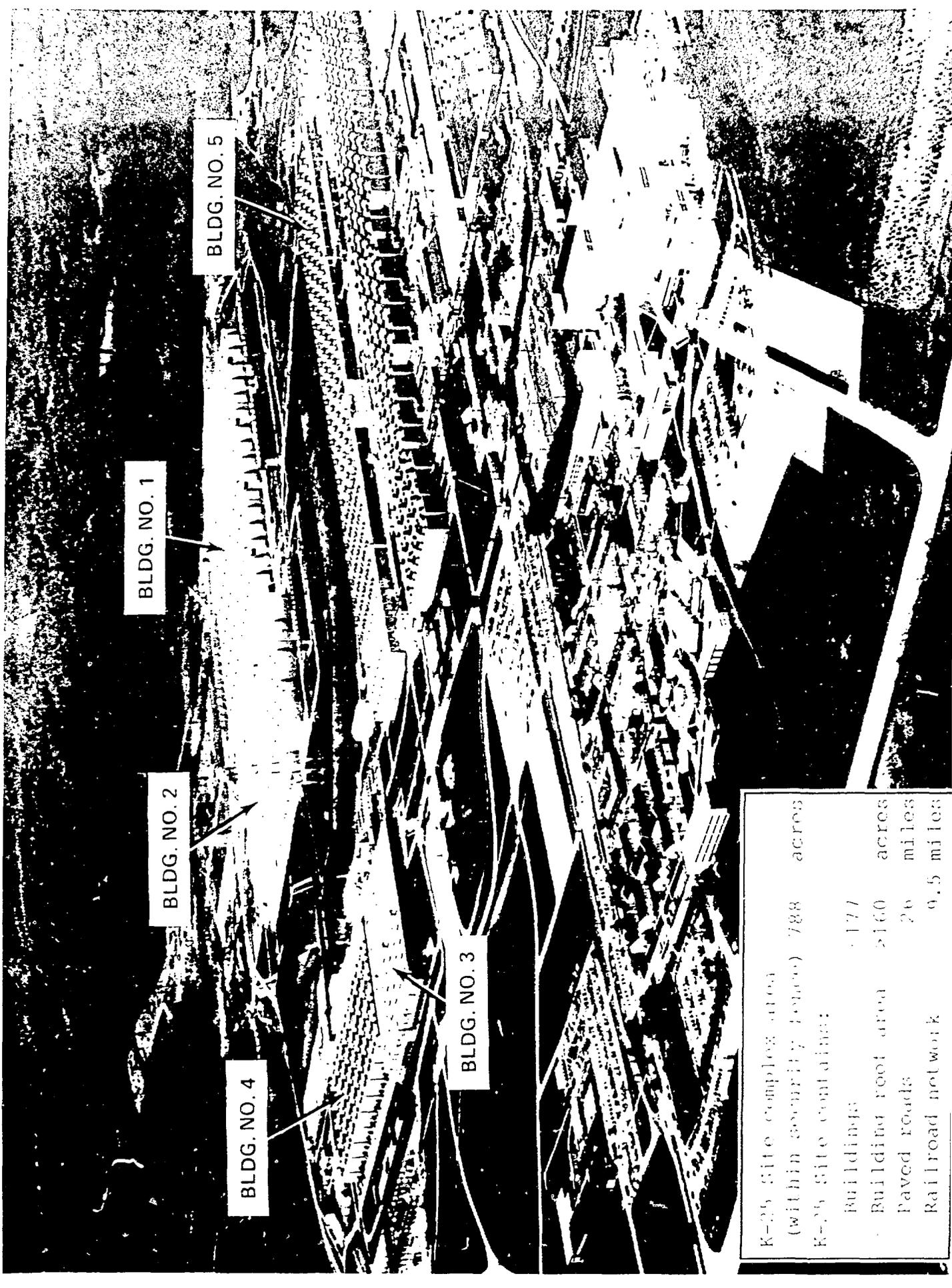
Air
Compressor

Converter

Control
Valve

Heat
Exchanger





BLDG. NO. 1

BLDG. NO. 2

BLDG. NO. 4

BLDG. NO. 5

BLDG. NO. 3

K-25 Site complex area (within security fence)	788	acres
K-25 Site contains:		
Buildings	177	
Building roof area	>160	acres
Paved roads	26	miles
Railroad network	9.5	miles

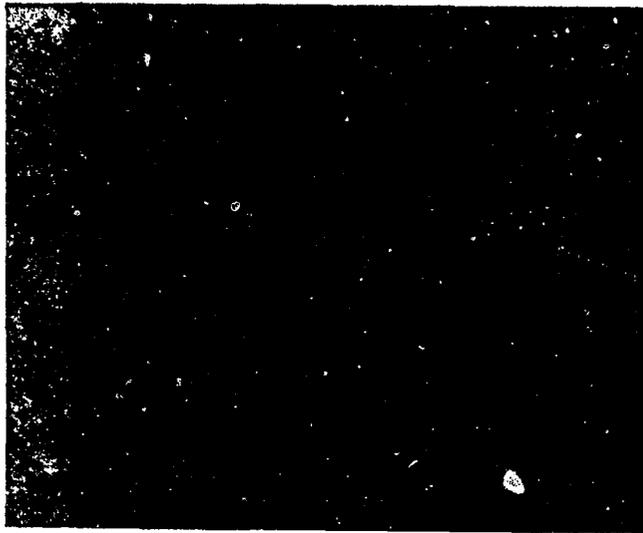


FIGURE 3 Typical "000" cell.



FIGURE 4 "000" Compressor.

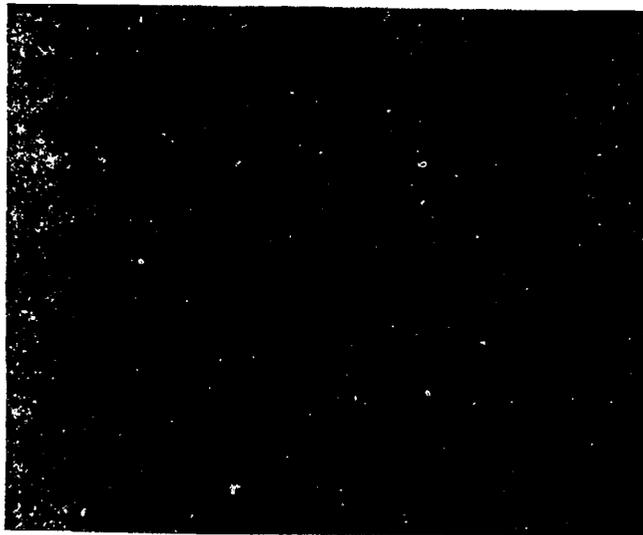


FIGURE 5 Centrifugal stage equipment.

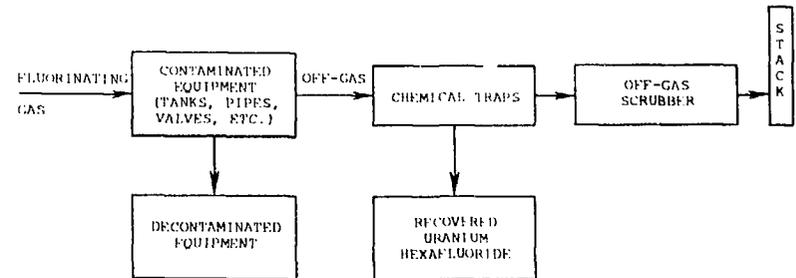
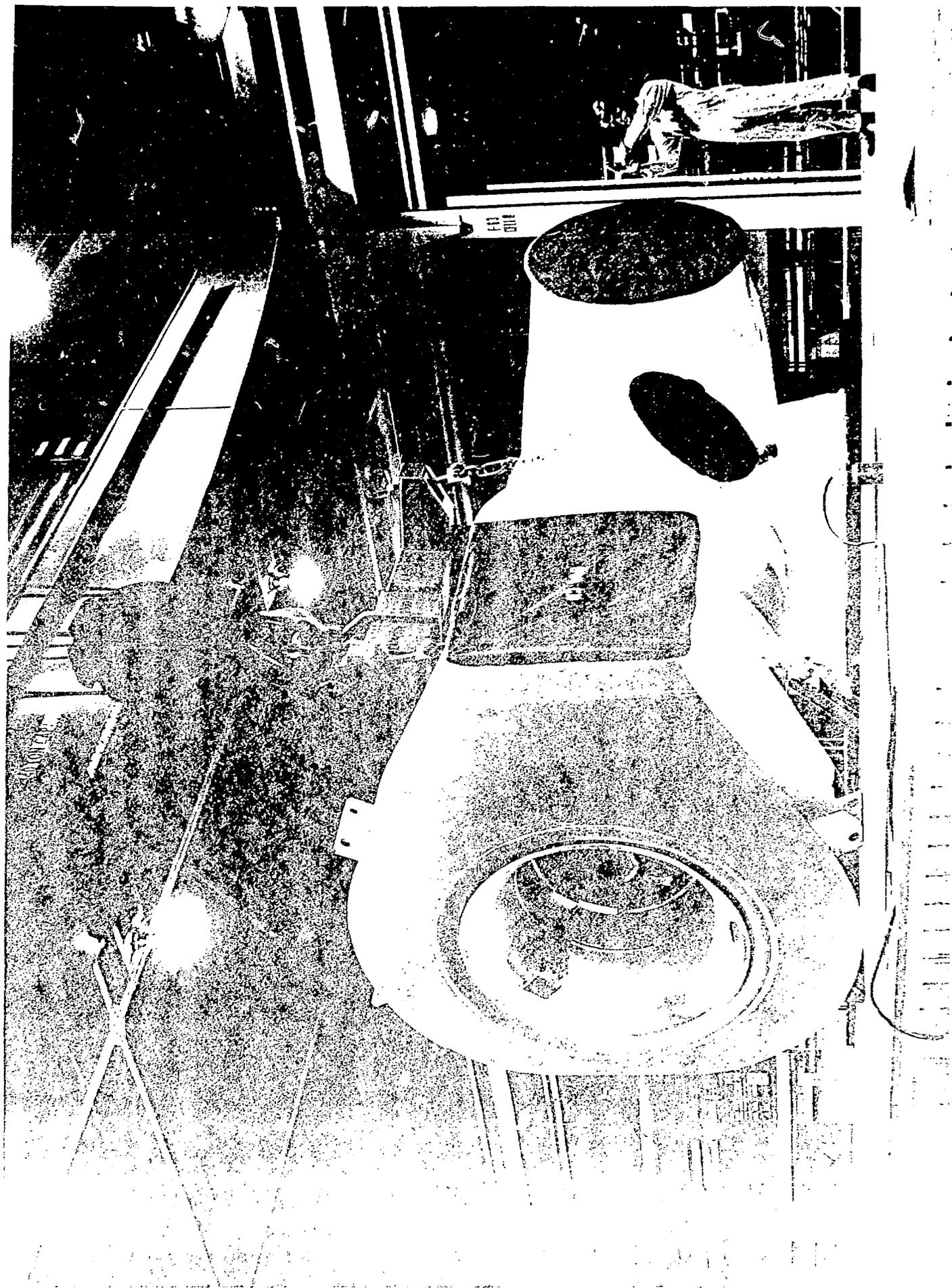


FIGURE 6 Concept of gas-phase decontamination.







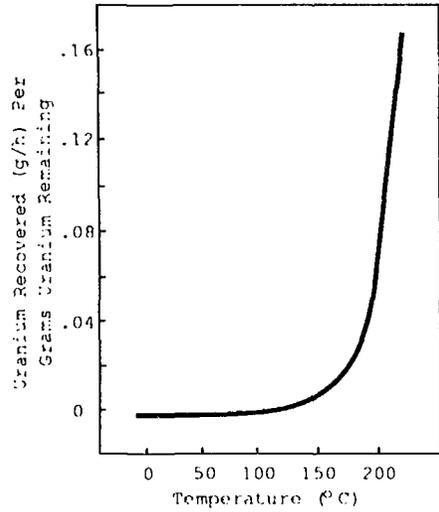


FIGURE 7 Temperature dependence of the F₂ reaction ⁵ uranium deposits (mainly UO₂F₂).

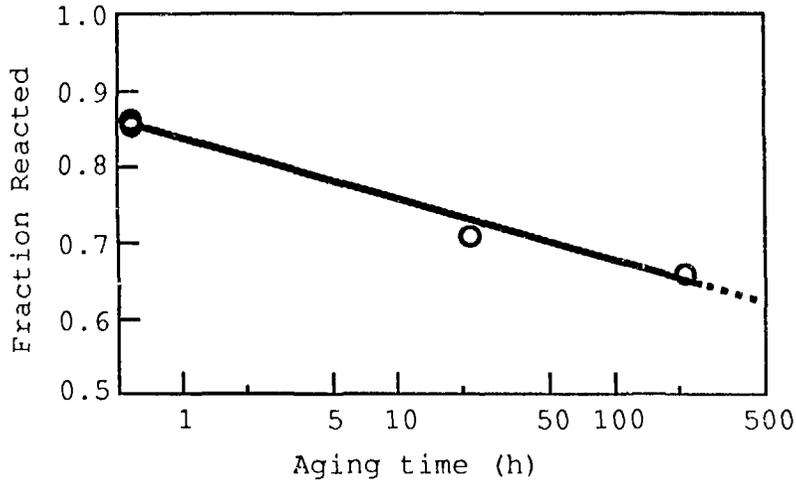


FIGURE 8 Fraction of UO₂F₂ reacted after 4h of reaction with ClF₃ versus aging of the UO₂F₂ sample. ⁶

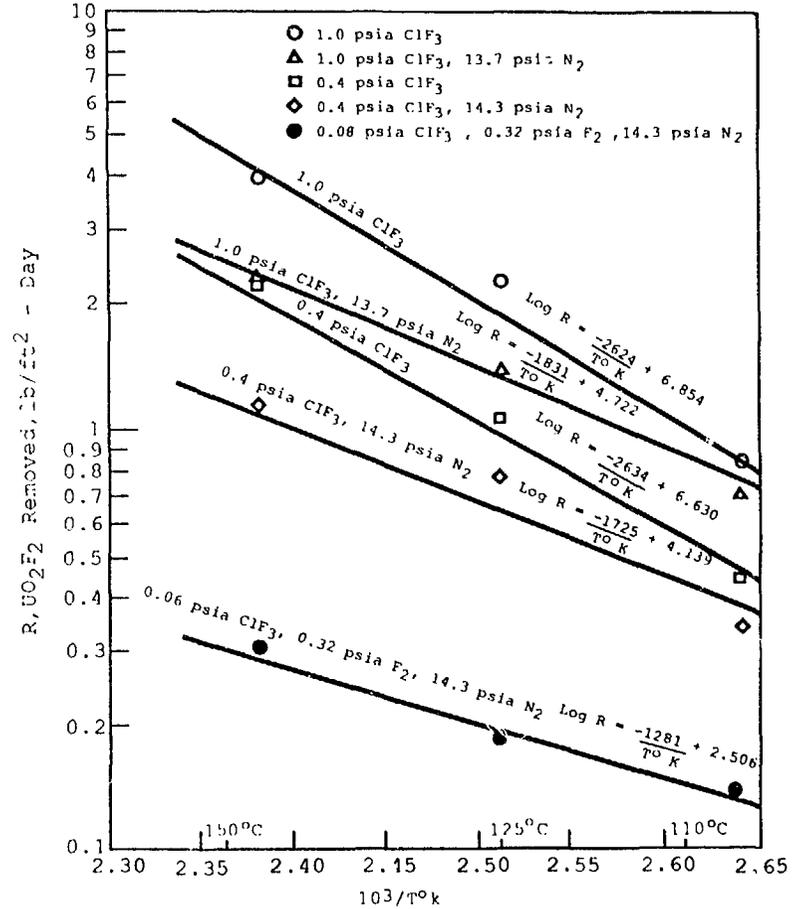


FIGURE 9 Temperature dependence of the UO₂F₂/ClF₃ ⁹ reaction.

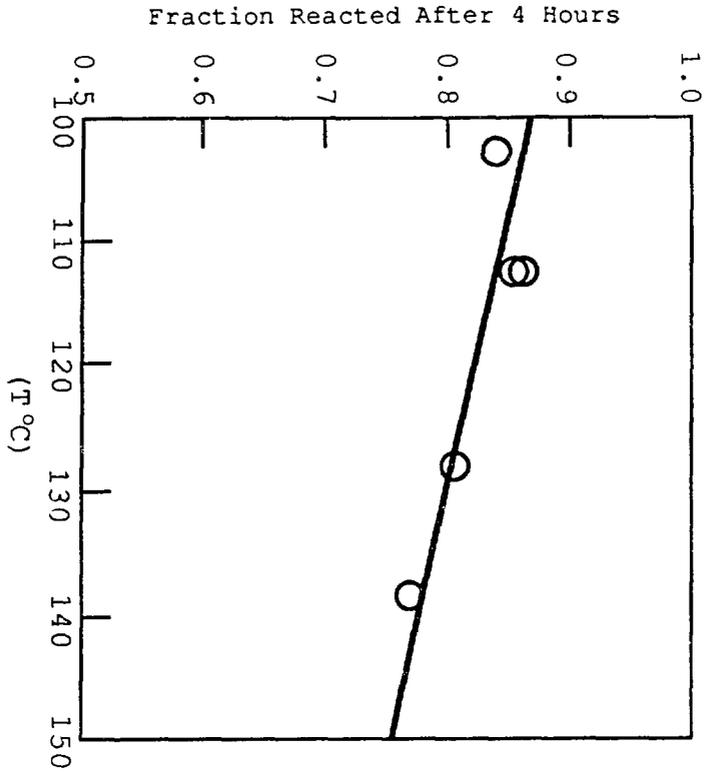


FIGURE 10 Temperature dependence of the UO_2F_2/ClF_3 reaction. 6

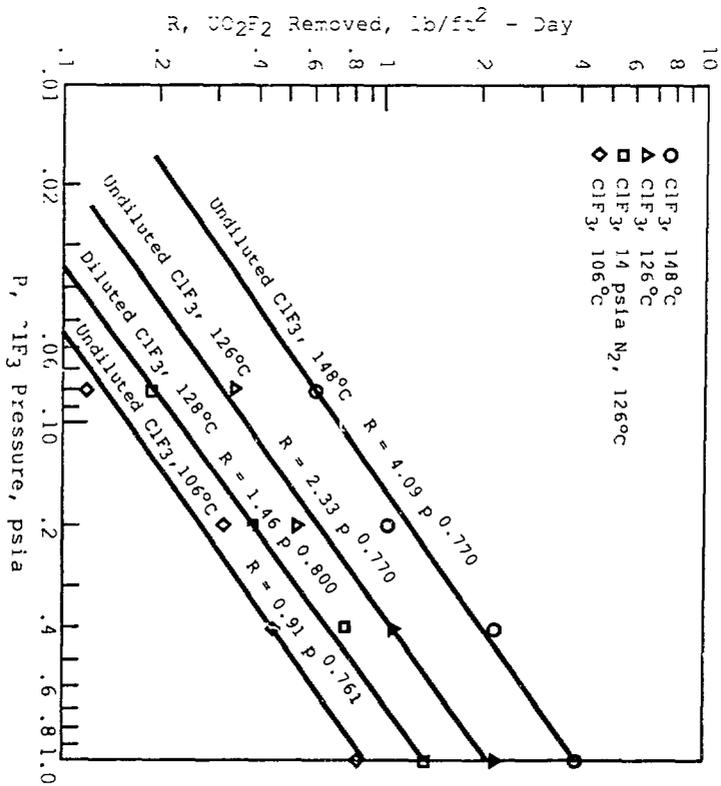


FIGURE 11 ClF_3 partial pressure dependence of the UO_2F_2/ClF_3 reaction. 9

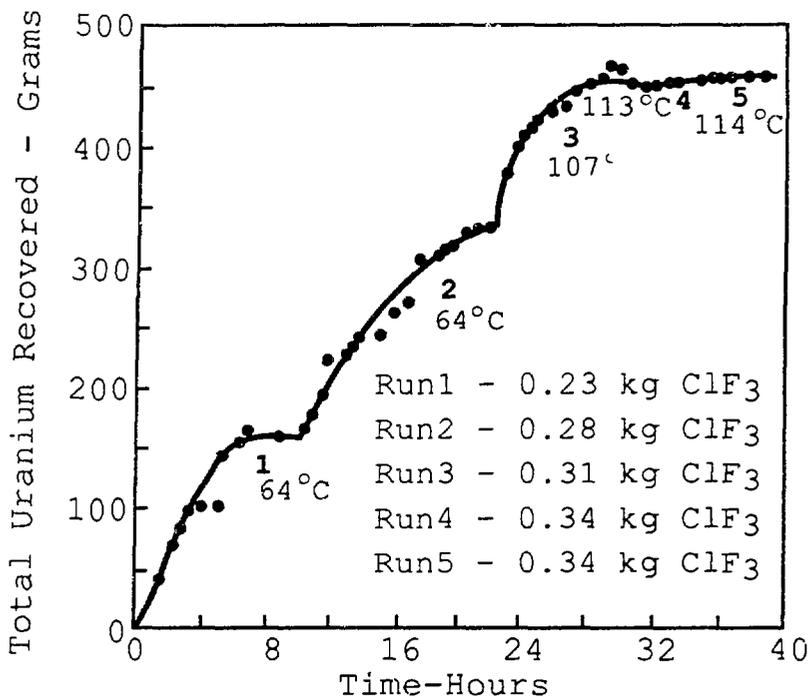


FIGURE 12 Uranium recovery versus time during ClF₃ decontamination of a converter. 12

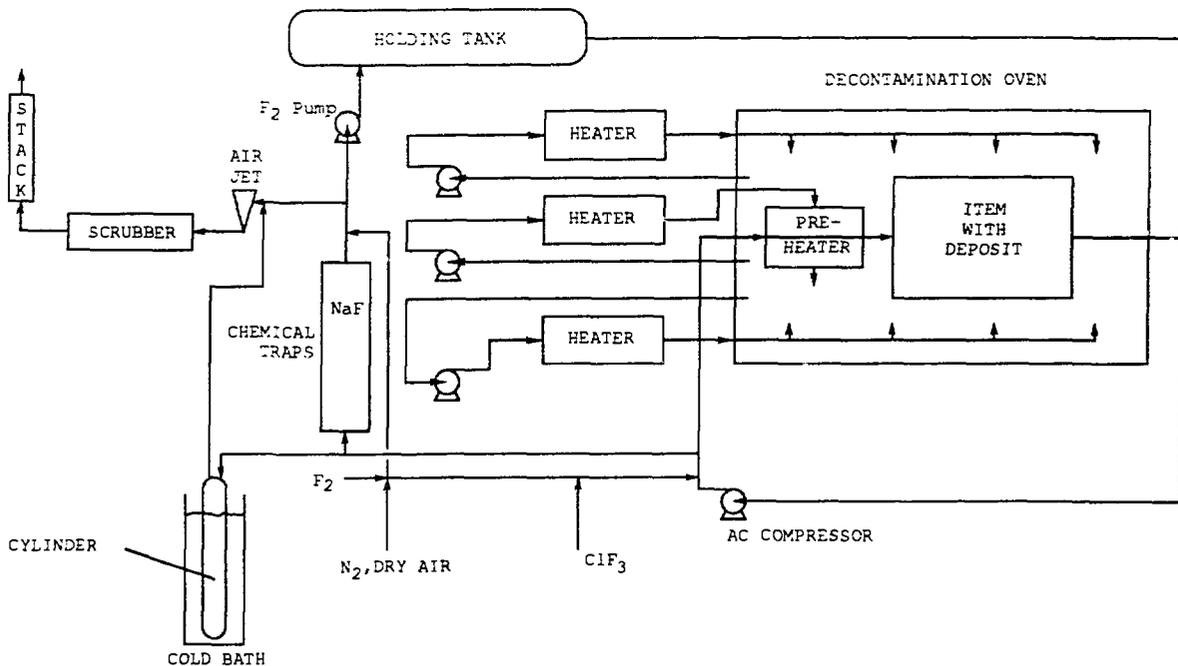


FIGURE 13 Simplified flow diagram for deposit removal in an oven.

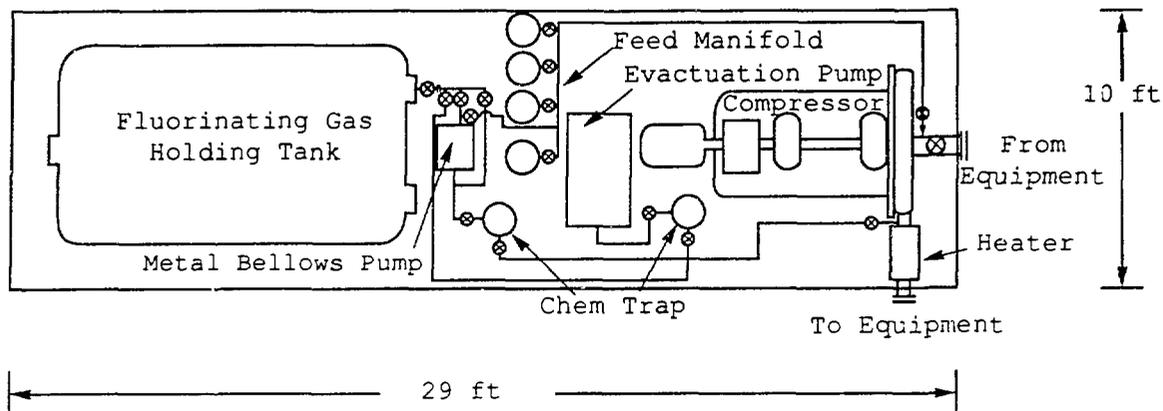


FIGURE 14 Equipment layout on a trailer for the proposed mobile gas phase decontamination system.

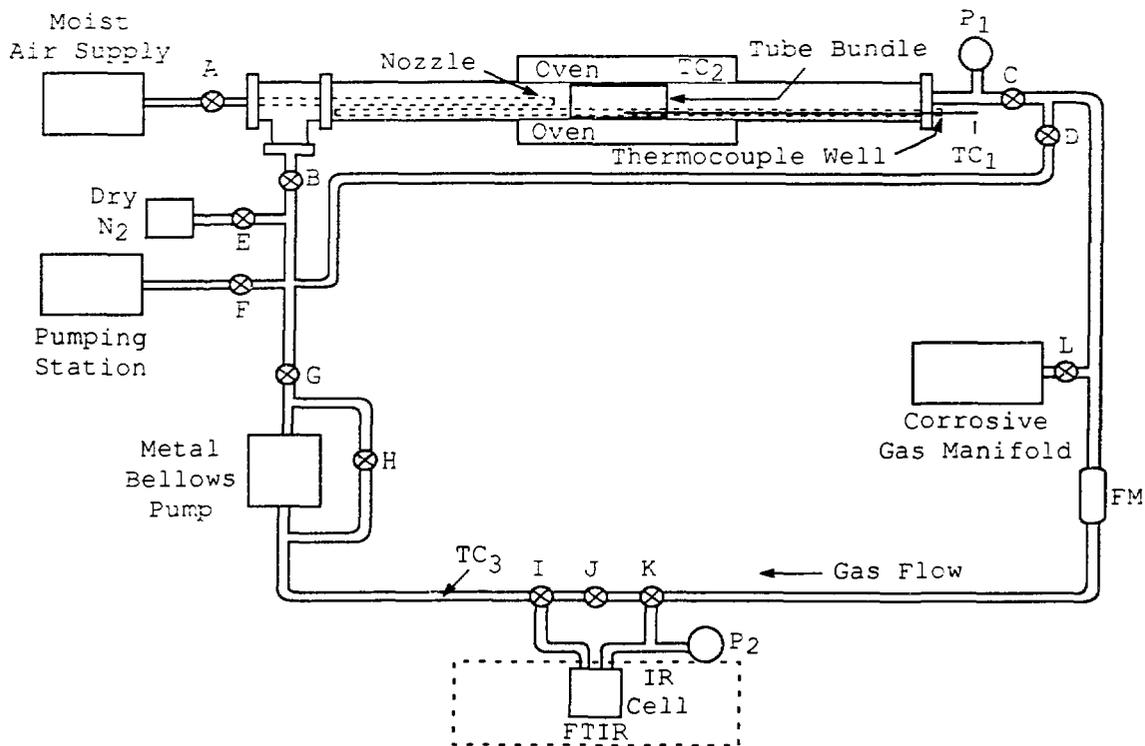


FIGURE 15 Schematic of laboratory scale test equipment. 2