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FLUORINE DISPOSAL

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A preliminary design of an F_2 disposal system for HELSTF is presented here along with recommendations on operational policy and identification of potential operational problems. The analysis is based on sizing a system to handle two different modes of the HELSTF Fluorine Flow System (one operational and one catastrophic). This information should serve both as a guide to a final detailed design for HELSTF as well as a reference for subsequent monitoring and/or modification of the system which consists of a charcoal reactor followed by a dry soda lime scrubber.

Contents

A. HELSTF F_2 FLOW SYSTEM - DISPOSAL DESIGN CRITERIA

Two cases were considered in the design of the waste disposal system:

1. TRW Pallet - consists of an 8.2 ft^3 sphere filled with F_2 at 450 psi with a 1" burst disk and approximately 80 feet of 1" tubing leading up to the disposal system. Treating F_2 as an ideal gas gives 25 lbs of F_2 stored in the vessel which could be dumped through the disposal system. The following equation was used to compute the emptying time (p. 482 of Transport Phenomena by Bird, Stewart, and Lightfoot):

$$t = \frac{V/S_2}{\sqrt{\gamma\left(\frac{p_o}{\rho_o}\right)\left(\frac{2}{\gamma+1}\right)^{\left(\frac{\gamma+1}{\gamma-1}\right)}}}\left(\frac{2\gamma}{\gamma-1}\right)\left(1-\left(\frac{\rho_1}{\rho_o}\right)^{\frac{\gamma-1}{2\gamma}}\right)$$

Where t = emptying time

V = volume of tank

S_2 = area of outlet

γ = Cp /Cv

p_o, ρ_o = initial pressure and density in tank

ρ_1 = final density

This gives an emptying time of about 8.4 seconds which is an average of 1697 scfm or approximately 3 lb/sec. Neglected here is the resistance in the line from the tank to the disposal system, therefore, these numbers represent an extreme worst case.

2. Aspirator - Composition of the F_2-N_2 mixture through the aspirator will vary; however, a 50-50 mixture by volume at 36 scfm will be taken as a typical starting condition. At .03 lb_m F_2/sec this would be 1/100 of the F_2 rate in the catastrophic case above.

B. LITERATURE REVIEW

For the purpose of summarizing several reports on F_2 disposal consider the following three step process to remove F_2 from gas streams:

Process Flow Scheme

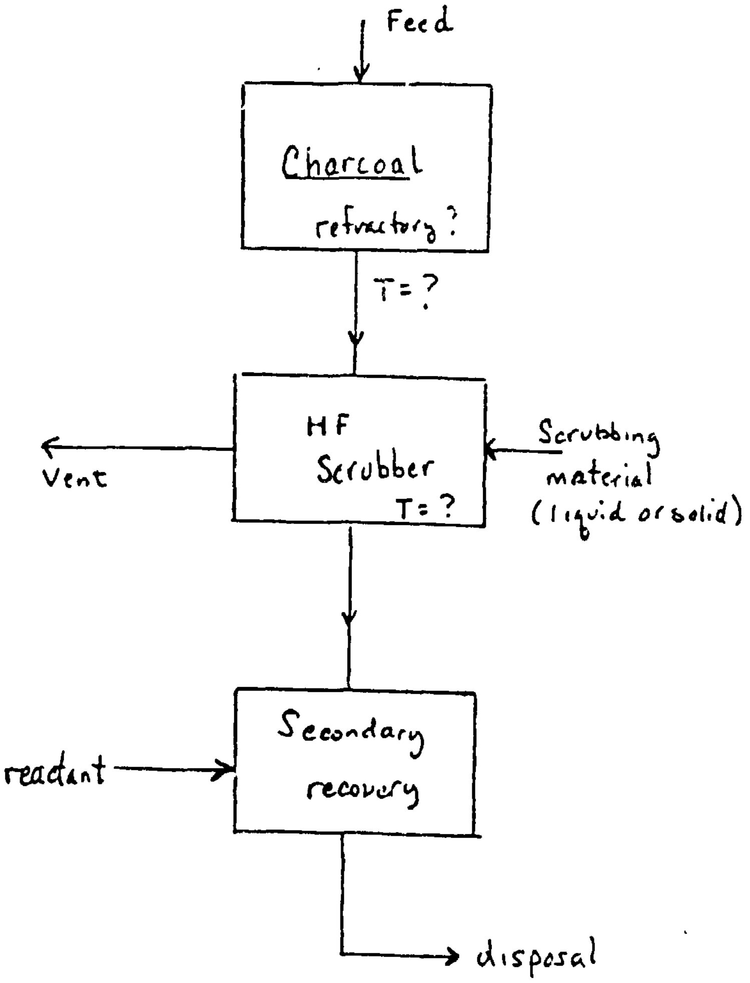

Table I is a summary of various designs and operating conditions. Note that KOH is a popular scrubbing fluid for HF. This is probably due to its greater solubility in H_2O then NaOH as well as a marked difference in solubility of KF vs. NaF in H_2O as shown in Table II. KOH would have a definite advantage over NaOH since a scrubber could run longer on recycled liquid before an insoluble salt would form. There are several disadvantages of a KOH scrubber; however, which would make a solid system more desirable. First, the scrubbing liquid would have to be treated in a secondary step to remove KF. Secondly, the freezing point of KOH would probably be in the 20-30^{0}F range which could cause problems since the system will be outdoors. Third, a packing material would be desirable to effect mass transfer, and lastly liquid handling equipment would be necessary. If a liquid system could be avoided this would be a great advantage.

Table II. Solubility* g/100 ml H_2O

NaOH	42^0
KOH	97^0
NaF	4.22^{18}
KF	92.3^{18}

*Handbook of Chemistry & Physics

TABLE I.

SOURCE	F_2 FEED CONC.	FEED RATE	CHARCOAL TYPE	SIZE OF REACTOR	REFRACTORY	EXIT T + COMPOSITION	SCRUBBING LIQ + RATE	VENT COND.	SECONDARY PROCESS	COMMENTS + PROBLEMS
Air Products 1983	High They make CF_4 Insulator, Refrigerant	Industrial	Granulated Carbon	?	?	2000°F Some F_2 Cryo Trap HF, for Economics	KOH (45%) Steel Tellerettes	2ppm HF?	for KF?	Industrial
Air Products 1983	?	Small	Briquettes	Portable - Design Available	? Cooling H_2O	Dump to Secluded Area	Scrubber Attached Solid Na_2CO_3	?	---	Portable for remote venting
Union Carbide 1975	$\leq$ 10% (mole)	$\leq$ 2000 $\frac{cc}{min}$	Wood, purified recommended different types tested	Lab Scale 2" x 14"	No	< 200°F < 650°F (heated)	---	<50 ppm	---	Pure charcoal needed to prevent non CF_4 fluorocarbon products. A lot of F_2 trapped in unreacted charcoal
NASA Lewis 1968	$\leq$ 100%	$\leq$ 61 $\frac{lbs}{hr}$	? 3/8"	6.7 ft^2	Yes	? 5-825 ppm	---	5-82. ppm	---	Insufficient Data
WADD Handbook 1960	?	?	---	---	---	---	NaOH Monel, egg size fluorspar packing	Good ?	---	Insufficient Data

TABLE I. (Continued)

SOURCE	F_2 FEED CONC.	FEED RATE	CHARCOAL TYPE	SIZE OF REACTOR	REFRACTORY	EXIT T + COMPOSITION	SCRUBBING LIQ + RATE	VENT COND.	SECONDARY PROCESS	COMMENTS + PROBLEMS
Air Force Kirtland 1978	---	---	---	---	---	---	Unknown Scrubber	---	---	No Info.
L. Livermoré 1972	?	?	?	1-1/3' x 2-1/3' ash removal port	Ceramic (3 inches) or Al_2O_3	?	KOH with KI to speed reaction	---	Recycle Liq.	
General Dynamics I 1971	Small-100%	3600 lb/hr max	---	---	---	---	KOH-10% 200 gpm 7 ft dia tank	< 1000 ppm ?	Neutralize KF with lime to make CaF_2	Claim Allied Chem has several yrs. success with system
General Dynamics - II 1971	?	9000 $\frac{lb}{hr}$ combustion rate	Graded Oak Min. ash and hydrocarbon	Twice stoichiometric	Firebrick vapor barrier over charcoal	? 2520°R max	$F_2 + H_2O \rightarrow HF + O_2$	Gas Velocity < 1 fps	$HF + CaCO_3 \rightarrow CaF_2 + H_2O + CO_2$	---

NASA Lewis strongly recommends a charcoal reactor for a first step and Air Products has developed a portable system (Figures 1 and 2) to handle small quantities of F_2 (dumping a single cylinder in a remote location). The Air Products system is an all solid system, i.e., Na_2CO_3 is used in the second stage to remove HF. Note also that the charcoal system has water cooling available since the heat of reaction is very high for $C+2F_2 \rightarrow CF_4$.

It should be noted that Union Carbide, as a result of a lab scale study ($< 10\%$ F_2 in N_2, < 2000 cc/min), recommended the purification of wood charcoal by heating to 850°C to eliminate the formation of precipitates from non-CF_4 fluoro carbons formed. In the same study they found that for dry charcoal and 1% F_2 in N_2 with no heat source other than heat of reaction conversion of F_2 to CF_4 was poor (5800 ppm F_2 in effluent). Whether these problems will appear at higher rates and concentrations is doubtful. Nevertheless, this information should be kept in mind should any problems arise in the charcoal reactor (they resorted to sintered metal filtering and heating the reactor to alleviate these problems).

H. Schmidt of NASA Lewis (Feb. 1959) concluded that "for engineering design approximations, the stoichiometric charcoal requirement is 17.5 pounds charcoal per 100 pounds of fluorine gas to be burned, plus minimum charcoal for maintaining reaction efficiency toward the end of the burning period." Also mentioned is "low F_2 flowrate through high capacity

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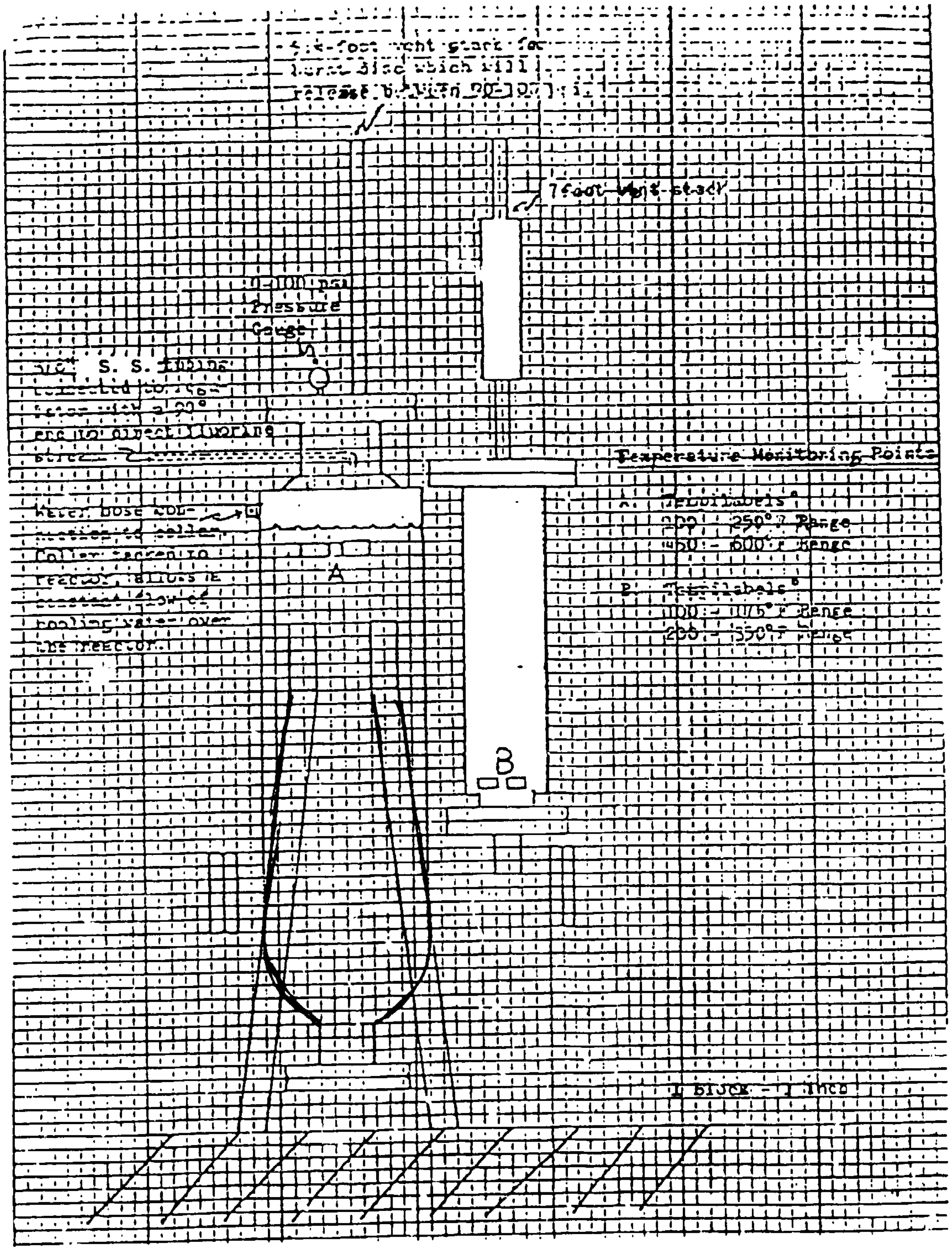
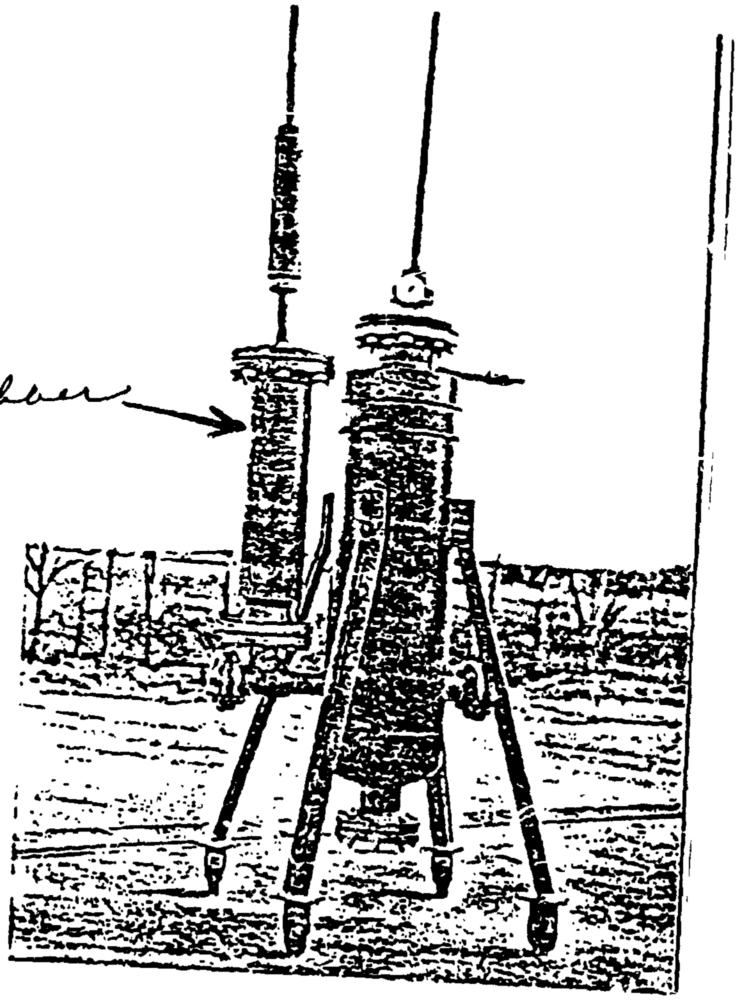


Fluorine Disposal Unit

Figure 1

Portable F_2 Disposal Unit



Scrubber

Figure 2

reactors has on two occasions allowed excessive heating of the F_2 inlet nozzles in uncooled reactors, causing F_2 attack on the nozzles and refractory lining in the lid. Higher flowrates through the nozzles provided sufficient cooling to prevent this attack. ..... in one test the equipment was operated at over 600 pounds per hour for approximately three minutes (equivalent to 30 lb F_2) ..... without damage to the reactor." One can conclude from this report that careful attention must be paid to the use of cooling to prevent damage to the system. In fact, it is also mentioned that "with a furnance grating support with bottom inlet feed, the reaction process tends to consume the grating."

NASA Lewis concluded that only the external surfaces of the charcoal particles are active in the reaction and that the controlling factor in the reaction is probably "mass transfer by counter diffusion of the reactants and products into and away from the solid surface through the gas layer." They then recommend the following as a design equation:

$$R = \frac{65V}{D} \quad \text{lb } F_2/\text{hr}$$

where $R = F_2$ rate in lb/hr - max allowable

V = charcoal volume, ft^3

D = particle diameter, in.

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Lastly, it should be mentioned that no attempt has been made here to review KOH liquid scrubbing since a solid bed system is recommended. An extensive literature exists in this area, however, should interest arise. Also, there are several industrial processes and patents by the Japanese, Russians, and Germans on F_2 removal which could be studied.

C. ANALYSIS

For the two cases described in Section A the following calculations are made:

1. Amount of charcoal required
2. Amount of soda lime required
3. Exit gas temperature from charcoal
4. Exit gas temperature from soda lime
5. Pressure drop thru charcoal and soda lime

1. Amount of Charcoal Required

a) TRW Pallet - From a stoichiometric point of view we have 25 lbs of F_2, therefore, we need":

$$25 \times \frac{17.5}{100} \quad 4.4 \ \underline{\text{lbs charcoal}}$$

If we were to use the NASA design equation $R = \frac{65V}{D}$ for

3/8" charcoal and a rate of 1697 scfm (10,780 lb/hr) we'd need 62 ft^3 of charcoal. Considering a void volume of .4 and a charcoal density of 12 lb/ft^3 this would be <u>446</u> lbs of charcoal.

We can also use the following equation to compute the volume of charcoal required to achieve a particular exit concentration of F_2 from the bed:

$$V = \frac{G}{akgC} \ln \left(\frac{Y_{A_1}}{Y_{A_2}} \right)$$

where V = volume of bed, ft^3

G = molar rate of gas, $\frac{\text{lb moles}}{\text{min}}$

a = effective surface area/vol of bed, $\frac{ft^2}{ft^3}$

kg = mass transfer coefficient, ft/min

C = molar density of gas = $\frac{P}{RT}$ = $\frac{\text{lb moles}}{ft^3}$

Y_{A_1} = mole fxn of F_2 into reactor

Y_{A_2} = mole fxn of F_2 out of reactor

This equation is based on steady isothermal flow and diffusion control, i.e., as soon as the F_2 reaches the charcoal surface it reacts instantaneoulsy with the carbon on the surface only.

For the TRW pallet case, $Y_{A_1} = 1$, $G = 4.73 \frac{\text{lb mole}}{\text{min}}$, $C = \frac{P}{RT} =$

$\frac{14.7 \text{ psi} \times 144}{1544\ (2000^0\text{R})} = .0007 \frac{\text{lb moles}}{\text{ft}^3}$ assuming a max T of 2000^0R in

the reactor, $a = 115 \frac{\text{ft}^2}{\text{ft}^3}$ for 3/8" particles

and set $Y_{A_2} = 1 \text{ ppm} = 10^6$

From Figure 3 we can take kg to be 10 cm/sec or 19.7 ft/min.

$$\text{so} \qquad V = \frac{4.73}{(115)\ (19.7)\ (.0007)} \ln 10^6$$

$$\text{or} \qquad V = 41.2 \text{ ft}^3$$

(not drastically different from the NASA design equation)

This would be 297 lbs of charcoal.

b) Aspirator

1) NASA Design:

$$18 \text{ scfm} \times \frac{1 \text{ lb mole}}{359 \text{ ft}^3} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{38 \text{ lb}}{\text{lb mole}} = 114 \frac{\text{lb}}{\text{hr}}$$

$$V = \frac{114}{65} \times \frac{3}{8} = .65 \text{ ft}^3 \quad (4.7 \text{ lb charcoal})$$

2) Diffusion Control Equation:

$Y_{A_1} = .5$, $G = .1 \frac{\text{lb mole}}{\text{min}}$

kg = 2 cm/sec = 3.94 ft/min

$$V = \frac{.1}{115\ (3.54)\ (.0007)} \quad \ln \frac{.5}{10^{-6}}$$

$V = 4.13\ ft^3$ (30 lb charcoal)

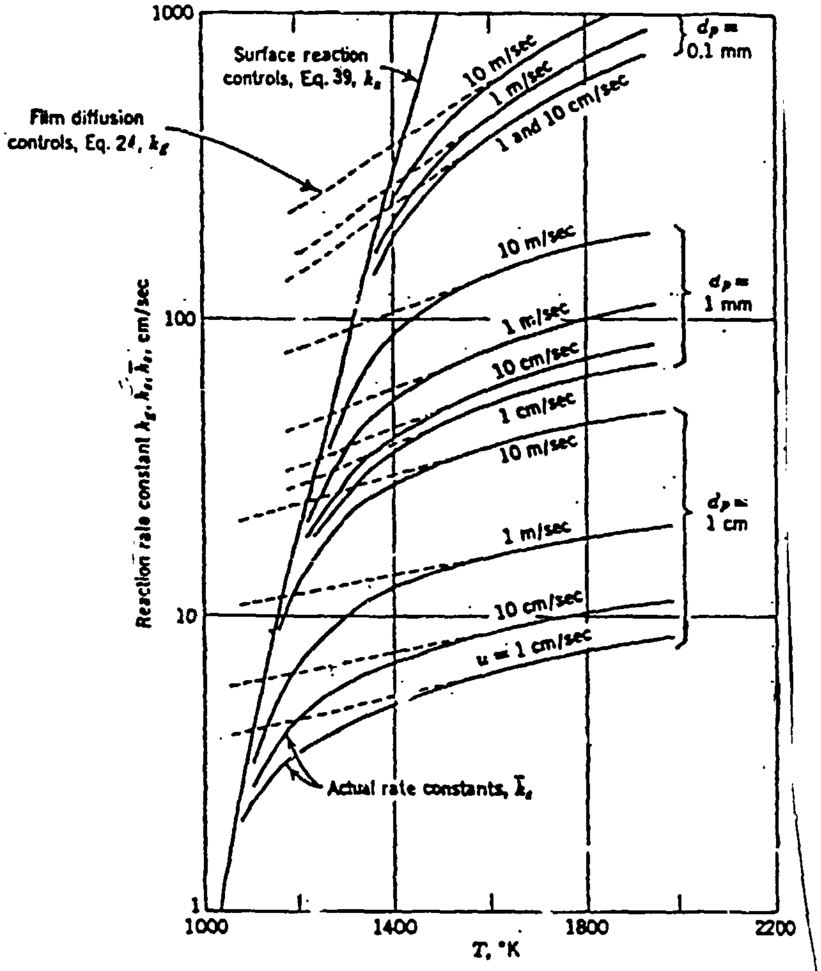

FIGURE 12. Rate of combustion of pure carbon particles, adapted from Yagi and Kunii (1955)

which the reaction kinetics, flow characteristics, and size distribution of solids are known.

Referring to Fig. 13, let us discuss briefly the various types of contacting in gas–solid operations.

Solids and Gas Both in Plug Flow. When solids and gas pass through the reactor in plug flow, their compositions will change during passage. In addition, such operations are usually nonisothermal.

Figure 3

2. Amount of Soda Lime Required

a) TRW Pallett - Assuming 10% HF out of the charcoal due to the residual H_2O in the charcoal and the same model (diffusion control) as the charcoal then:

$$Y_{A_1} = .1$$

$$a = 445 \frac{ft^2}{ft^3} \text{ for 1/8" soda lime particles}$$

$$G = 2.36$$

Since there are half as many moles of gas ($C+2F_2 \rightarrow CF_4$) then:

$$V = \frac{2.36}{445\ (19.7)\ (.0007)} \ln \frac{.1}{10^{-6}}$$

$$V = 4.42\ ft^3$$ (at a density of 125 $\frac{lbs}{ft^3}$ and a void fraction of .4 this would be 331 lbs of soda lime

b) Aspirator

$$\frac{4.42}{41.2} \times 4.13 = .44\ ft^3 \rightarrow 33 \text{ lbs of soda lime}$$

3. Exit Gas T From Charcoal

a) TRW Pallet - We'll assume that an equilibrium is established whereby the charcoal temperature rises to that of the exit gas and the system is adiabatic (no transfer through walls).

The heat of reaction of $C + 2F_2 \rightarrow CF_4$ is 222 kcal/g mole.

$$\frac{25 \text{ lbs } F_2}{38 \text{ lbs/lb mole}} \times \frac{454 \text{ g mole}}{\text{lb mole}} \times \frac{222 \text{ kcal}}{\text{g mole}} = 66,308 \text{ kcal}$$

$$C_p \text{ carbon} = \frac{.387 \text{ cal}}{g^oC}$$

$$C_{p_{gas}} = .25 \frac{\text{cal}}{g^oC}$$

$$66,308,000 = (446 \text{ lbs charcoal})(454 \frac{g}{lb})(.387)(\Delta T) + 25(454)(.25)(\Delta T)$$

$$\Delta T = 816^oC = 1469^oF$$

If the F_2 comes in at $70^oF \rightarrow$ exit T = 1530^oF or $\sim 2000^oR$

b) Aspirator

Basis: 10 minutes of operation

$$\frac{18 \text{ scfm} \times 10 \text{ min}}{359} = .5 \text{ lb moles}$$

$$.5 \times 454 \times 222 = 50,394 \text{ kcal}$$

With the small quantity of charcoal required for this system it is clear that extremely high temperatures would be reached (of course, it is really necessary to know exactly the inlet F_2 concentration during aspiration to pin this number down).

Therefore, it is apparent that the system required for the TRW pallet case should be used for the aspirator as well to prevent excessive temperatures!

4. EXIST GAS TEMPERATURE FROM SODA LIME

a) TRW Pallett - Treating .1 lb mole HF with 331 lbs of soda lime would give a $\Delta T = 407^{\circ}F$. This would result in a temperature of about $2000^{\circ}F$ out of the soda lime (if there were no cooling between the charcoal reactor and soda lime system).

b) Aspirator - not considered.

5. PRESSURE DROP THRU CHARCOAL

a) TRW Case

Ergun equation:

$$\frac{\Delta P}{z} \; \frac{g_c \varepsilon^3 \, dp \, \rho_g}{(1-\varepsilon) \, G'^2} = \frac{150 \, (1-\varepsilon)}{R_e} + 1.75$$

where $\frac{\Delta P}{z}$ = pressure drop per unit length of packed bed

ε = void volume

d_p = diameter of particles

ρ_g = gas density

G' = superficial mass velocity - mass/(area x time)

R_e = $dp \, G'/\mu$

μ = viscosity of gas

For the TRW case with a reactor 4' x 4' x 4':

$$G' = \frac{25\ \text{lbm}}{8.4\ \text{sec}} \times \frac{1}{16\ \text{ft}^2} = .186\ \frac{\text{lbm}}{\text{sec ft}^2}$$

$$dp = 3/8''/12 = \frac{1}{32\ \text{ft}} \qquad \varepsilon = 0.4$$

$$\rho_G' = \frac{(14.7)\ (144)\ (38)}{(1544)\ (2000)} = .026\ \frac{\text{lbm}}{\text{ft}^3}$$

$$\mu \simeq 7\ \text{lbf}\ \frac{\text{sec}}{\text{ft}^2} \times 10^{-9}$$

$$R_e = \frac{\frac{1}{(32)}\ (.186)}{(7\times10^{-9})\ (32)} \approx 26{,}000 \qquad [\text{1st term negligible}]$$

$$\therefore \quad \frac{\Delta P}{z}\ \frac{g_c\ \varepsilon^3\ dp}{(1-\varepsilon)\ G'^2}\ \rho_g = 1.75$$

$$\frac{\Delta P}{z} = \frac{(1.75)\ (.6)\ (.186)^2}{(32.2)\ (.4)^3\ (1/32)\ (.026)} = 21.7\ \frac{\text{lbf/ft}^2}{\text{ft}}$$

$$\frac{\Delta P}{z} = .15\ \text{psi/ft}$$

ΔP = .6 psi (add a bit more [1 psi total] for soda lime)

b) Aspirator - Not considered.

D. PROPOSED SYSTEM DESIGN

1. Charcoal Reactor - A volume of 62 ft^3 (446 lbs of wood charcoal, 3/8" diameter) is required. The General Dynamics Sycamore Canyon Reactor (GDSCR) would be a suitable design. It is basically a cylindrical furnace with a firebrick floor, firebrick walls of 4-1/2 in. x 9 in. straights and wedges, and a conical sheet metal hood. Since the GDSCR was designed for 528 cu ft with 2 ft of ullage above the charcoal the GDSCR could be scaled down by 1/3 in cross-sectional area and 1/3 in height to give the required HELSTF volume. The inlet and outlet lines will of course be smaller but the inlet should be equipped with cooling water and the polyethylene isn't needed since the HELSTF system will be used for normal operation. Attached is a description of the GDSCR system.

2. Soda Lime Scrubber - A volume of 4.42 ft^3 (331 lbs) is required. Fischer Chemical (Wendy 800/527-5920) can supply 14 kg containers (6-12 mesh) at $135 per container. This amount should be sufficient for each aspiration. The design for this system could be the same as the GDSCR only scaled down to the smaller volume.

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GDSCR SYSTEM DESCRIPTION

Distribution of fluorine flow in a charcoal charge cannot assure stoichiometric combustion. The reactor is therefore designed to hold twice the theoretically required charge of charcoal, giving sufficient bed depth to prevent channeling and blow-through, take care of ash content, and provide a safety margin. Nominally designed for disposal of 20,000 pounds of fluorine boiled off from the vehicle tank in an emergency, the reactor is also capable of handling the 30,000 pounds of fluorine in the storage tank, if necessary.

Density of graded oak charcoal, with a minimum ash and hydrocarbon content, is approximately 12 lb/cu ft. Theoretical volume of charcoal required for the reactor unit, Eq. 3-1, is therefore:

3160 lb ÷ 12 = 264 cu ft

or 528 cubic feet with the double volume for allowances. A 9-ft. dia. cylindrical chamber 15 feet in height is adequate for the volume required, including a 28-in. ullage above charcoal level.

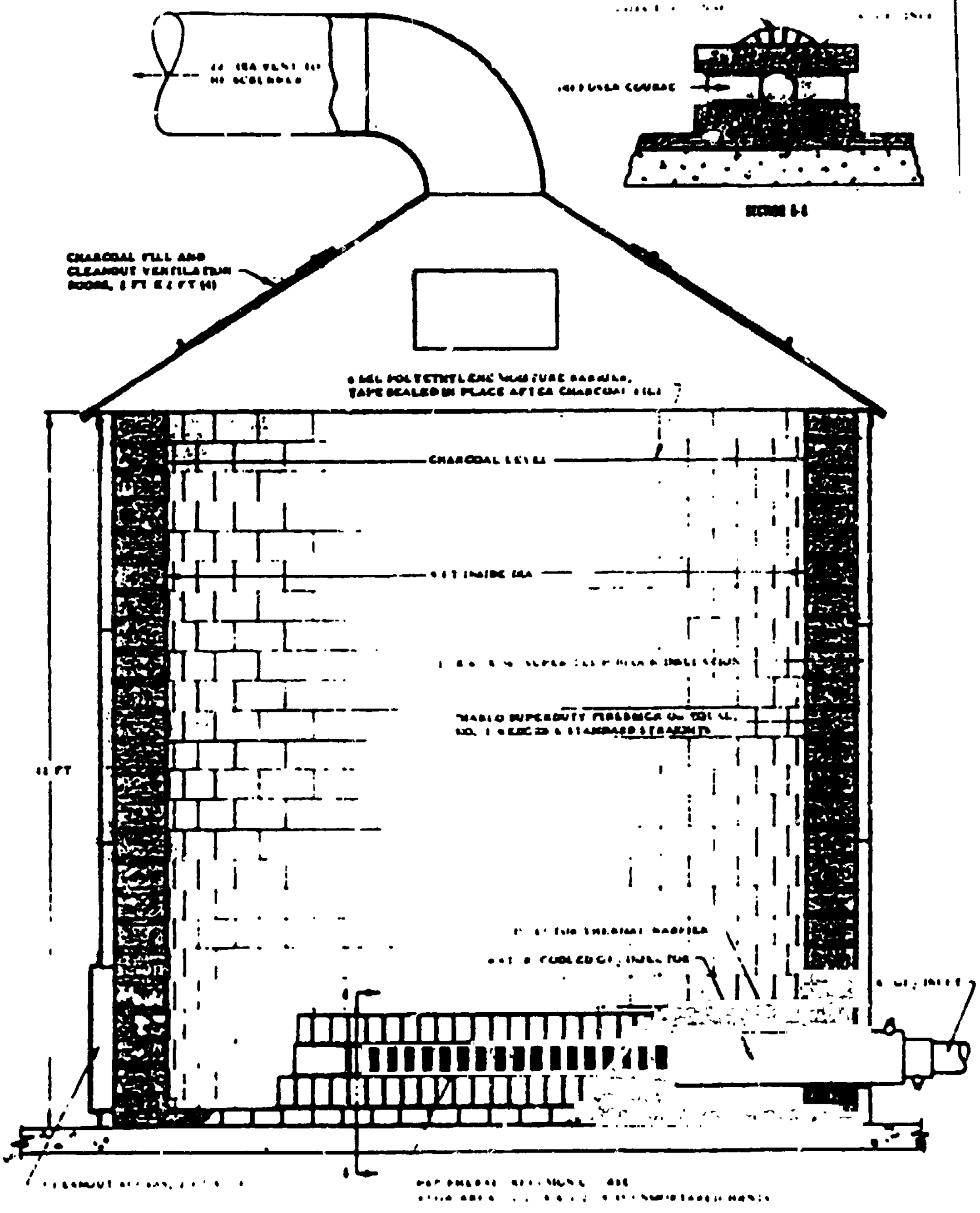
The reactor unit is shown in cross-section in Figure 3-15. It is basically a cylindrical furnace with a firebrick floor, firebrick walls of 4 1/2-in. × 9-in. straights and wedges, and a conical sheet metal hood. Gaseous fluorine is introduced through a 6-in. inlet, water-jacketed and protected from furnace heat by a firebrick injector tunnel, or igloo. Diffusion of fluorine into the charcoal is through a three-course diffuser as shown in Section A-A, Figure 3-15. The top and bottom courses are mortared. The intermediate course is recessed, with the vertical joints unmortared for fluorine egress. This is the final configuration of the fluorine injection system of the General Dynamics Sycamore Canyon reactor, successfully used for disposal of gaseous FLOX from Atlas vehicle tank tests.

The hood of the reactor is fitted with four 2-ft × 2-ft swing-doors for charcoal loading and ventilation during cleanout. If the reactor is ever used, it is refurbished by first opening the ground-level cleanout access door and knocking out a firebrick soft patch. With the upper doors open for ventilation, ash and excess charcoal can be removed through the lower door. After cleaning and inspection, the access opening is refirebricked, the door closed, and the furnace charged with charcoal through the upper loading doors. After charging, the charcoal is leveled and a 4-mil polyethylene vapor-barrier sheet laid in place and taped, to exclude atmospheric humidity and retain the charcoal in a dry state.

The burner vent line is sized for a maximum combustion rate of 9000 pounds of fluorine per hour, producing 2.9 pounds of CF_4 per second. The 20-in. dia. line delivers combustion products at a maximum velocity of 30 fps to the scrubber.

Estimated cost of the reactor unit is $7,500, including fabrication of the water-cooled injector, sheet-metal work, and labor.

GDSCR SYSTEM DESIGN



E. RECOMMENDATIONS

1. Measure F_2 and HF concentrations in effluent during test run to confirm efficiency of system (temperature would also be useful).

2. Use extreme caution in cleaning and replenishing system (after 10 aspirations) since fluorine could be present.

3. Should cooling water be unavailable make sure that F_2 metal inlet tube is replaced with refractory.

4. Same approach should be taken with soda lime scrubber.

5. System requires 3/8" wood charcoal, should particle entrainment become a problem consider adding a filter between the charcoal and soda lime reactors.