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ABSTRACT

Tests were made to determine the type of charcoal and operating parameters best suited for fluorine disposal. Nonactivated wood charcoal was found to be safe in operation, and heating of the charcoal to ∿300°C was necessary for efficient reaction of fluorine. At low fluorine concentrations (<25% F_2 in the gas stream), the principal reaction product is a white fluorocarbon smoke. CF_4 is the principal product with 100% fluorine. A small amount of condensable fluorocarbons is formed by the fluorine-charcoal reaction.

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INTRODUCTION

Safe disposal of waste gases containing elemental fluorine is a common problem among industries using this very reactive and toxic gas. Most of the common methods, such as caustic scrubbing, burning, chemical conversion to chlorine by reaction with sodium chloride, and reaction with activated alumina, form byproducts that also present disposal problems.[1] One of the simplest and most economical methods of fluorine disposal is based on the reaction of wood charcoal with fluorine to produce nontoxic fluorocarbons, which can be vented to the atmosphere. The primary product of the reaction between fluorine and charcoal is CF_4 with small amounts of higher fluorocarbons.[2] Heated[2] and unheated[3] charcoal traps have been used at several sites for fluorine disposal.

Standifer et al.[4] have used activated wood charcoal in unheated traps for fluorine disposal. Pulley and Harris[5] recommended nonactivated wood charcoal heated to 125-300°C. Explosions were reported with activated charcoals and low fluorine concentrations. The explosions were attributed to the rapid reaction of a large quantity of adsorbed fluorine with charcoal after the reaction was initiated by increasing the fluorine concentration.[5] This hypothesis was confirmed by several observations:

- Nonactivated charcoals with low surface areas (and thus lower capacity for fluorine adsorption) did not explode when reacted with fluorine under the same conditions.

- The residual fluorine concentration in unreacted activated charcoal was much higher than that in nonactivated charcoal.

- Fluorine adsorbed on activated charcoal could be removed by purging; then the charcoal did not explode when the fluorine concentration was sharply increased.

Published data do not adequately define trap operating conditions, such as temperature and fluorine flow, for efficient fluorine disposal. Data for the composition of reaction product gases at various operating conditions are also incomplete. The present study was undertaken to clarify these uncertainties.

EVALUATION OF CHARCOALS

APPARATUS

Several types of wood charcoals and sintered coke were tested for fluorine disposal in the apparatus shown in Figure 1. Charcoal was supported by nickel screens in a nickel column 0.87 inch in diameter and 12 inches long. A calibrated Hastings-Raydist mass flowmeter (Model LF-1K) was used to measure fluorine flow. Nitrogen flow was measured with a calibrated rotameter. Fluorine-nitrogen mixtures were passed through a baffled mixing chamber before reaction with charcoal. Unreacted fluorine in the charcoal column effluent was reacted with activated Al_2O_3 or, in some cases, with 0.5M KI in a countercurrent scrubber. Thermocouples strapped to the outside wall of the column were used to monitor temperature. In some tests, the column was heated with clamshell heaters.

CHARCOAL PROPERTIES

Properties of charcoals tested are given in Table I. Charcoals received as large lumps were ground and sieved to size. Charcoals 6 and 7 were purified from traces of volatile hydrocarbons by heating at 950°C in a nitrogen purge, as recommended by Pulley and Harris.[5] Sintered coke, a hard, brittle material, was also tested because of its low surface area. Surface areas of charcoals were measured by the nitrogen absorption method.

TESTS WITH UNHEATED BED

As-received charcoals were tested in an unheated column with a bed depth of 10 to 12 inches. Nitrogen and fluorine (5-100%) were passed through the column to determine maximum flow without appearance of fluorine in the effluent (breakthrough) and to determine steady-state operating temperatures. Fluorine breakthrough is caused by incomplete reaction of fluorine with charcoal at low temperature and high flow. Fluorine breakthrough was determined with KI-saturated paper, which can detect fluorine at >25 ppm.

Charcoals 1 and 2 (activated wood) reacted with fluorine with no breakthrough, but water driven from the fluorine-charcoal reaction zone and charcoal fines increased the pressure drop across the bed. Charcoals 3 and 4 (nonactivated wood) reacted with fluorine

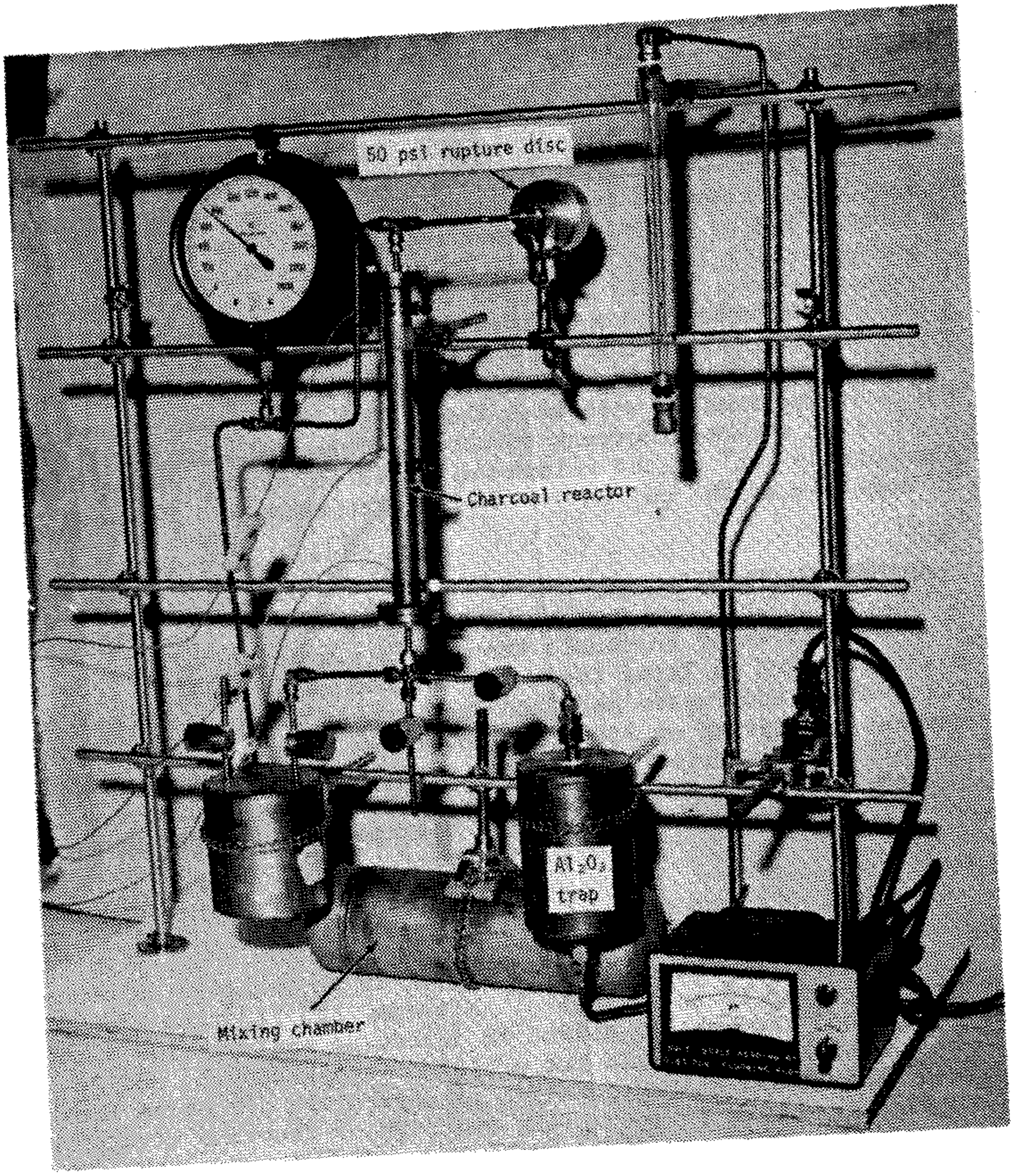

FIGURE 1. Apparatus for Fluorine-Charcoal Tests

TABLE I

Properties of Charcoals Tested for Fluorine Disposal

Number	Type	Vendor	Mesh Size	Bulk Density, g/cc	Surface Area, m^2/g	Carbon, %	H_2O, %
1	Activated wood	Barneby-Cheney	4-8	0.34	580	89.0	6-12
2	Activated wood	Barneby-Cheney	2-4	0.27	485	89.0	5-10
3	Nonactivated wood	Barneby-Cheney	4-8	0.23	170	79.9	2-4
4	Nonactivated wood	Roseville Charcoal Co.	2-8[a]	0.21	93	77.1	1.5
5	Nonactivated wood	Connecticut Charcoal Co.	2-8[a]	0.29	3	73.6	0.5-1
6[b]	Nonactivated wood	Roseville Charcoal Co.	2-8	-	144	94.6	-
7[b]	Nonactivated wood	Connecticut Charcoal Co.	2-8	-	12	93.7	-
8	Sintered coke	Union Carbide	2-8	-	3	75.3	-

[a] Received from vendor as large lumps; ground and graded to size.

[b] Purified by heating for 3 hr at 950°C in a N_2 purge.

and prevented breakthrough until the bed dried, at which time the charcoal was very inefficient for fluorine disposal. In previous study,[5] similar results with nonactivated wood charcoals were reported. During these tests, the 1/4-inch-diameter outlet line from the column periodically became plugged with condensable fluorocarbons formed by the incomplete reaction of charcoal with fluorine.

TESTS WITH HEATED BED

Additional fluorine disposal tests were made with a heated charcoal bed. During a test with charcoal 1 (activated wood), an explosion occurred that burst the 50 psi rupture disc (with no further damage). Before the explosion, the column was heated to 200°C, and 4% fluorine was passed through the bed for ~20 minutes. The fluorine concentration was then quickly increased to ~10%, and the explosion occurred. There was a large quantity of charcoal fines in the bed after the explosion. Charcoals 1 and 2 were not considered further because of the explosion hazard. Tests were made with charcoals 3, 4, and 5 at the same conditions that caused charcoal 1 to explode; none of these samples exploded.

Table II summarizes the results of other tests with a heated column. These results demonstrate that nonactivated wood charcoals should be heated to >200°C for efficient fluorine disposal at low fluorine concentrations. At an initial temperature of 300°C, no fluorine breakthrough occurred with a 10- to 12-inch-deep charcoal bed even at very high flows. Sintered coke did not react appreciably with fluorine below 400°C.

TABLE II

Summary of Fluorine Disposal Tests in Heated Charcoal Trap

			Fluorine Breakthrough Conditions	
Charcoal Sample[a]	F_2, %	Initial Bed Temperature, °C	Gas Feed Rate, cc/min at ∿1 atm, 25°C	Superficial Gas Velocity, ft/min[b]
4	5	100	<300	<3.2
4	15	100	<180	<1.9
4	25	100	<200	<2.1
4	50	100	<140	<1.5
4	100	100	∿100	∿1.1
4	5	200	290	4.0
4	15	200	680	9.3
4	25	200	700	9.5
4	50	200	800[c,d]	>11[c,d]
4	100	200	800[c,d]	>11[c,d]
4	0.5	300	>7,000[c]	>117[c]
4	1	300	>6,000[c]	>100[c]
4	5	300	>10,000[c]	>167[c]
4	15	300	>4,700[c]	>78[c]
4	50	300	>600[c,d]	>10[c,d]
4	100	300	>600[c,d]	>10[c,d]
5	1	100	<1,000	<11
5	5	100	<300	<3.2
5	1.5	200	∿1,000	∿13.6
5	1	250	∿4,500	∿68
5	1	300	>10,000	>167
7	1	100	<1,000	<11
8	25	400[e]	∿1,000	∿20

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a. See Table I.

b. At bed top surface at beginning of run (initial bed temperature).

c. No breakthrough observed.

d. Flow not increased further because temperature reached 600°C.

e. At <400°C, sample 8 was not efficient for fluorine disposal.

Tests were made to quantify the effect of temperature on fluorine disposal with nonactivated wood charcoal (using charcoal 4). A scrubber consisting of a 1-inch-diameter, 4-ft-long glass column filled with hemicylindrical stainless steel packing was connected to the outlet of the charcoal column to trap unreacted fluorine. A 0.5M KI solution was pumped at ∿250 ml/min countercurrent to the gas flow ($N_2 + F_2$) in the scrubber. Saturated KI paper was used to determine that gas leaving the scrubber contained <25 ppm fluorine. Fluorine trapped by KI in the scrubber was determined with a calibrated fluoride-sensitive electrode.

Results (Table III) indicate that the fluorine-charcoal reaction efficiency increases with temperature. At 5% fluorine in the inlet gas, only ∿10% of the fluorine reacted with charcoal at 200°C. As indicated in Table II, a total flow >25 times higher than in these tests resulted in no fluorine breakthrough at 300°C and 5% fluorine.

The effect of charcoal bed depth on F_2 disposal rate was not determined in these tests. However, a previous study[2] demonstrated efficient F_2 disposal with 25% fluorine in a heated charcoal bed, 2 inches in diameter and 2.5 inches deep, at a linear flow of ∿150 ft/minute. At ≥300°C, the F_2-charcoal reaction zone is narrow, and high disposal rates can be attained until most of the charcoal bed is consumed.

TABLE III

Effect of Temperature on Fluorine Disposal
With Nonactivated Wood Charcoal (Number 4)

F_2 Concentration, %	Initial Bed Temperature, °C	Total Gas Flow ($N_2 + F_2$), cc/min	% F_2 Reacted With Charcoal
5	25	395	10.3
10	25	365	42.7
5	100	395	42.5
10	100	395	42.7
15	100	395	42.6
25	100	400	46.2
5	200	395	81.4
10	200	365	48.5
5	200	800	41.7
10	200	800	32.9
15	200	800	33.3
25	200	800	33.0

In all of the tests with a heated column, the 1/4-inch-diameter exit line was heated to ∿200°C to prevent condensation of solid fluorocarbons. The solid residue was a crosslinked fluorocarbon polymer with a molecular weight >2000.[5] The fluorocarbon residue melts at 130-150°C and is sufficiently soluble in "Freon"* PCA to be easily removed.

CHARCOAL UTILIZATION EFFICIENCY

Tests were made to determine utilization efficiency for several nonactivated wood charcoals, and also to determine the amount of condensable fluorocarbons formed per gram of charcoal consumed. Prior to the tests, the charcoals were dried at ∿110°C. A weighed amount of charcoal was reacted with 25% fluorine for 1 hr with the column initially at 300°C. Condensable fluorocarbons were collected in an air-cooled condenser filled with copper shot. At the end of the test, unreacted charcoal was weighed, and the amount of charcoal consumed per gram of fluorine was calculated. The condenser was reweighed to determine the amount of fluorocarbons collected. A portion of the fluorocarbons, other than CF_4, and C_2F_6, is noncondensable and passes through the condenser as a white smoke.

Results (Table IV) indicate that charcoals 4 and 6 are most efficient for reaction with fluorine. Charcoal efficiency is apparently unrelated to internal surface area (Tables I and II).

TABLE IV

Charcoal Consumption and Residue Formation

Charcoal Sample[a]	Number of Determinations	g F_2 per g Charcoal	Charcoal Efficiency,[b] %	g Condensables per g Charcoal Consumed
3	1	4.5	71	0.01-0.02
4	7	5.9 (avg)	93	0.01-0.03
5	4	4.0 (avg)	63	∿0.01
6	1	6.2	98	0.03

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[a] See Table I.

[b] Based on 6.33 g F_2/g C for the reaction $2F_2 + C \rightarrow CF_4$, and assuming the charcoals were 100% ^{12}C. Obviously the noncarbon impurities in charcoals 4 and 6 react with F_2; otherwise, the calculated efficiency could not exceed the carbon content (Table I).

* Du Pont trademark for fluorocarbons

All of the charcoals generated a measurable quantity of fluorocarbons that condense at room temperature. The differences in amount of condensables collected (Table IV) are not considered significant. Purified charcoal (sample 6) generated essentially the same amount of condensed residue as the other charcoals even though the carbon content of purified charcoal was much higher. The amount of condensable fluorocarbon formed is significant. A condenser or other collector located downstream of the charcoal trap could collect these fluorocarbons and should prevent line pluggage if the line between the charcoal trap and the collector were heated to ∿200°C. Downflow traps may be better than upflow because of possible fluorocarbon reflux in the latter.

ANALYSIS OF REACTION PRODUCT GASES

PROCEDURE

Gases formed by the reaction of fluorine with nonactivated wood charcoal at 300°C initial trap temperature were investigated. Nonactivated wood charcoal was heated, in the nickel apparatus used in the previous tests, to 300°C before fluorine flow was started. Fluorine flow was maintained at 250 cc/min, and N_2 flow was adjusted to obtain the desired F_2 concentration. The wall temperature of the reactor increased from 300 to 430°C with 10% F_2 feed, and from 300 to 565°C with 100% F_2 feed.

Samples of reaction product gases were collected in flow-through tubes and analyzed by gas chromatography. The chromatography was calibrated with CF_4, C_2F_6, C_3F_8, N_2, and CO_2; sensitivities for these gases were 0.07, 0.13, 0.25, 0.07, and 0.05%, respectively. A small amount of HF was formed, but no HF analyses were made because the results would depend on the dryness of the charcoal.

RESULTS

Results of the gas analyses are shown in Table V. Less than a detectable amount of CF_4 and only a small amount of C_2F_6 were formed with 10% F_2 at 41 ft/min inlet velocity. At these conditions, the predominant product is a white fluorocarbon smoke. Part of this smoke condenses at room temperature and has been identified as a crosslinked fluorocarbon polymer with a molecular weight >2000.[5] The amount of CF_4 and the CF_4/C_2F_6 ratio in the reaction product increased as the fluorine concentration was

TABLE V

Composition of Charcoal-Fluorine Reaction Product Gases

Nonactivated Wood Charcoal; Initial Temperature 300°C

Inlet Gas		Reaction Product Gases			
Superficial Velocity, ft/min[a]	$F_2:N_2$	CF_4, %	C_2F_6, %	CO_2, %	CF_4/C_2F_6
41	10:90	<0.07	0.4	3.1	<0.2
16.5	25:75	9.2[b]	1.1	2.3	8.4
5.9	70:30	50.5	3.1	2.8	16.3
4.1	100:0	87.7[c]	3.5	8.8	25.1

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[a] At 300°C

[b] Averages of analyses from four independent tests.

[c] Averages of analyses from three independent tests.

increased and velocity was decreased. Both factors tend to increase temperature (more heat of reaction with less gas flow to remove the heat) and drive the F_2-charcoal reaction to completion, i.e., formation of CF_4.

Ruff[6,7] reported increased conversion of charcoal to CF_4 at higher temperatures and fluorine concentrations. Houston[2] reported a slight increase in CF_4 formation at lower fluorine flows. The composition of reaction product gases agrees fairly well with those of Ruff,[6,7] except no C_3F_8 was observed in these tests.

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