GAT-T-819

MASTER

FLUORINE DISPOSAL USING CHARCOAL

N. W. Houston

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GOODYEAR ATOMIC CORPORATION
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FLUORINE DISPOSAL USING CHARCOAL

by

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SUMMARY

Fluorine diluted with nitrogen was reacted in a 2-inch diameter reactor with wood, coke, and coconut shell charcoals to determine the relative efficiencies of the charcoals for fluorine disposal. Feed containing 15, 30, and 45 per cent fluorine (by volume) was introduced to the reactor at rates of 10 and 20 scfh. and caused reactor wall temperatures of 600 to 1200°F. The reaction products were primarily inert fluorides of carbon with small amounts of fluorine (0.03 per cent or less) and hydrogen fluoride (1.10 per cent or less). It was found that all three types of charcoal were equally efficient for fluorine removal. However, the coconut shell charcoal produced the smallest amount of solid and liquid reaction products and therefore caused the least fouling of the reactor exhaust line.

The coconut shell charcoal was also tested in a 5-inch diameter reactor with feed containing 25 per cent fluorine. The flow rates were varied from 100 to 400 scfh., and the reactor wall temperatures ranged from 1200 to 1800°F. Removal of fluorine was as efficient as that accomplished with the 2-inch reactor.

INTRODUCTION

A corrosive and toxic gas such as fluorine should not be indiscriminately vented to the atmosphere. Vent gases at GAT which contain fluorine are routed through alumina traps or through Feed Plant clean-up reactors to reduce the fluorine concentration to the plant allowable limit of 0.1 ppm., by weight. National Aeronautics and Space Administration (NASA) has reported that fluorine and charcoal react to form non-corrosive, non-toxic fluorides of carbon which could be safely vented.[1,2]

An investigation was initiated to determine the adaptability of this method of fluorine disposal to the needs at GAT. The first phase of the project was carried out using a 2-inch diameter reactor. The information gained from these tests was used in setting up conditions and designing equipment for the 5-inch diameter reactor tests.

For safety reasons these tests were carried out in the Explosion Test Facility. Early literature (about 1934) indicated that an explosive substance, carbon monofluoride, would be formed when carbon contacted elemental fluorine.[3] NASA reported no explosions during their test and none were experienced in the course of this investigation.

EQUIPMENT DESIGN

The pilot plant was designed and built in the Explosion Test Facility with Monel and nickel as the materials of construction, except for the nitrogen metering system. Monel is very resistant to fluorine and HF corrosion.[4,5] Independent nitrogen and fluorine metering stations (refer to Figure 1) were provided to ensure accurate control of fluorine concentrations in the feed stream to the reactor. The control room of the Explosion Test Facility is shown in Figure 2.

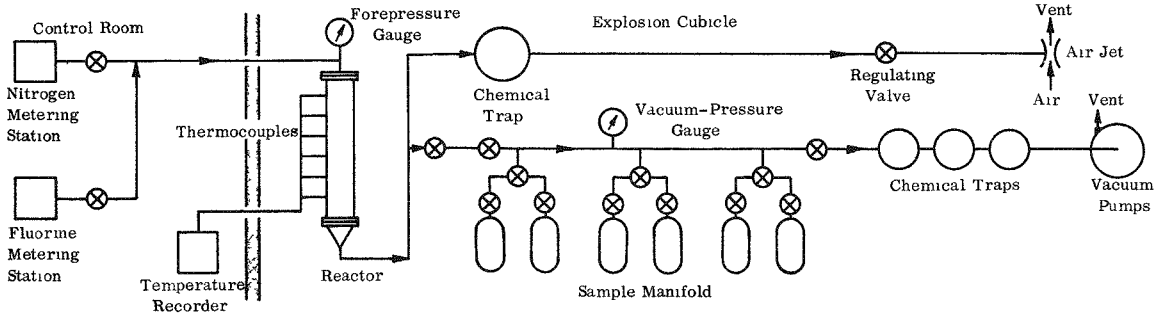


FIG. 1. FLUORINE-CHARCOAL REACTOR PILOT PLANT

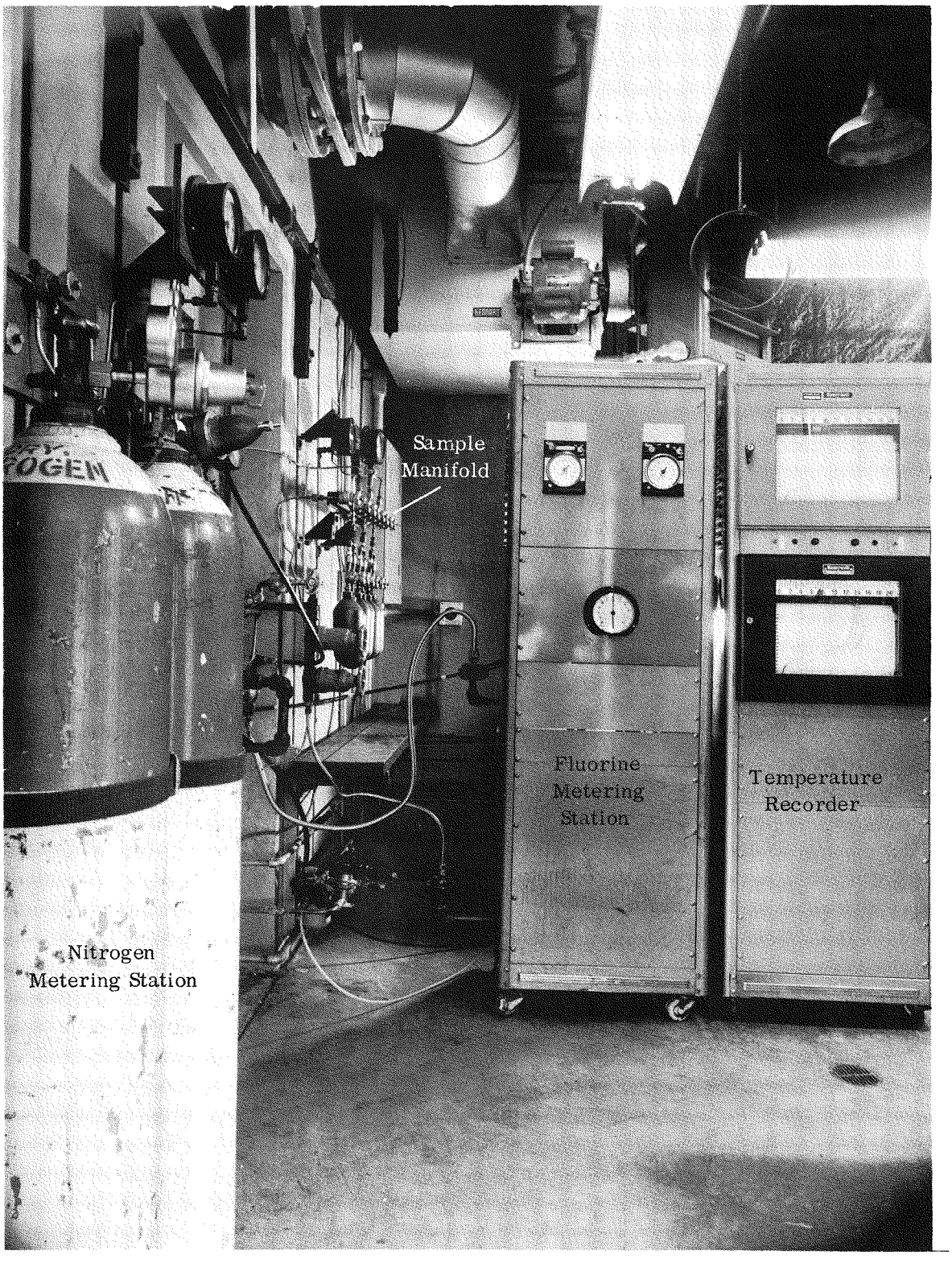


FIG. 2. CONTROL ROOM OF EXPLOSION TEST FACILITY

The reactor was fabricated from a 2-inch Monel pipe, 16 inches long. A 20-mesh Monel screen was inserted at the lower flange to support the charcoal bed, and a remotely controlled sample valve was installed in the reactor exhaust line. A sample manifold was constructed to permit withdrawal of duplicate samples from the reactor exhaust stream. A vacuum pump was located in the explosion cubicle (Figure 3) to evacuate the sample manifold and the sample containers. In order to simplify operation of the equipment, the pilot plant was designed so that the reactor could function at atmospheric pressure. An air jet and a regulating valve were used to control the reactor pressure. Chemical traps were installed in the reactor exhaust line and in the sample exhaust line; these traps were filled with alumina and soda lime for the removal of fluorine and hydrogen fluoride, respectively.

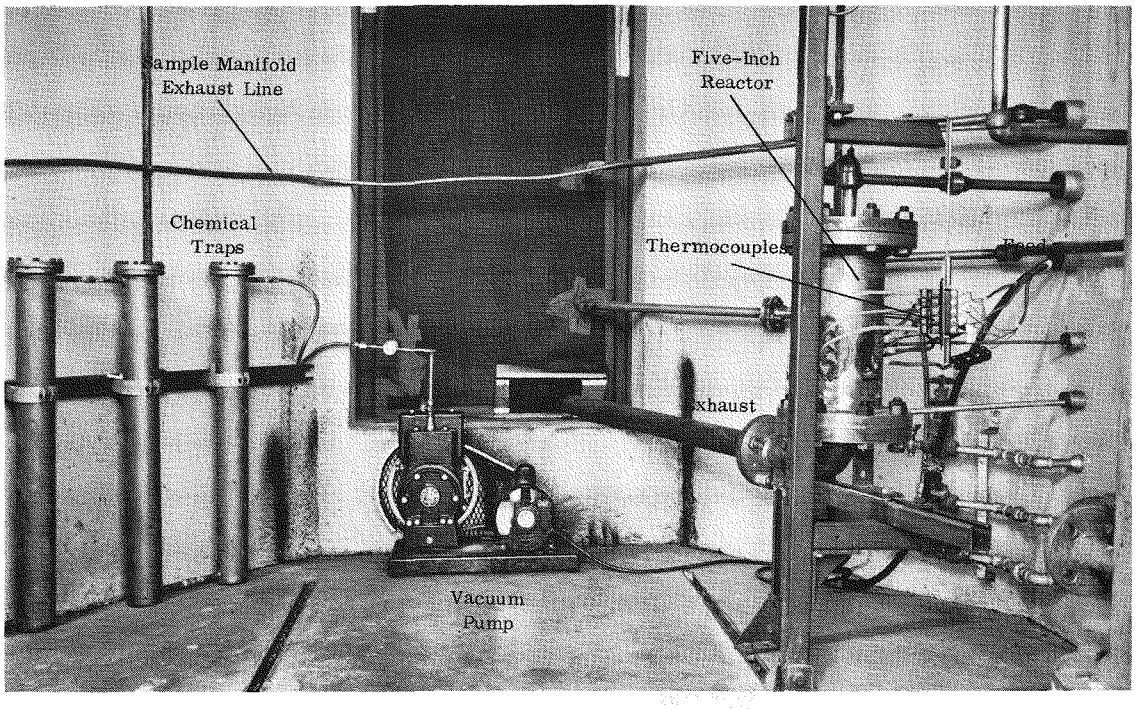


FIG. 3. EXPLOSION TEST FACILITY CUBICLE

PROCEDURE

The test procedure was established on a statistical basis wherein three types of charcoal of three mesh sizes were tested with three fluorine concentrations in the feed stream. The following latin square was used in order to obtain the necessary information with a minimum number of runs.

	C_1	C_2	C_3
BC	L (1)	M (2)	F (3)
PC	M (4)	F (5)	L (6)
W	F (7)	L (8)	M (9)

C_1 = 15 per cent fluorine in feed stream.
C_2 = 30 per cent fluorine in feed stream.
C_3 = 45 per cent fluorine in feed stream.
BC = Barnebey Cheney Type CG-2 (made from coconut shells)
PC = Pittsburgh Coke and Chemical Type BPL (made from coal)
W = Low grade wood charcoal
L = Large size (7 - 10 mesh)
M = Medium Size (12 - 16 mesh)
F = Fine size (30 - 40 mesh)

For example, a run using Block No. 7 would involve fine mesh wood charcoal and a fluorine concentration of 15 per cent in the feed stream.

Analyses of the charcoals used for the tests are shown below.

	Fixed Carbon, %	Volatile Matter, %	H_2O, %	Ash, %
BC Type CG-2	91.3	4.1	2.1	2.5
PC Type BPL	69.0	14.4	10.7	5.9
Wood, common	71.2	23.8	1.2	3.8
BC Type 4815	75.3	14.2	8.8	1.5
BC Type 4816	82.6	8.4	4.9	3.9

TWO-INCH REACTOR TESTS

Preliminary runs were made in order to become familiar with operation of the equipment and it was found that the air jet was not needed to maintain atmospheric pressure in the reactor. All three types of charcoal ignited spontaneously at room temperature with feed streams containing 5 per cent fluorine (10 scfh. total flow), and the reaction proceeded smoothly. The reaction temperature was a function of the amount of fluorine in the feed stream as shown in Figure 4. During a run with Barnebey-Cheney CG-2 charcoal, several "pings" were heard in the reactor. These "pings" were probably caused by incompletely charred charcoal, containing volatiles, which burst when subjected to heat. Several incompletely charred fragments were found on the upper flange of the reactor at the end of the run.

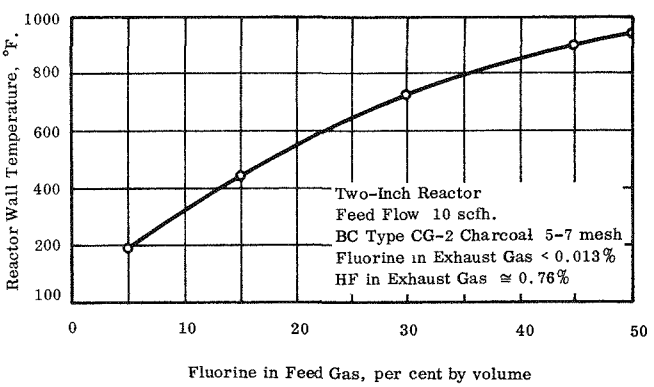


FIG. 4. REACTOR WALL TEMPERATURE VS FLUORINE CONCENTRATION

The first series of tests consisted of nine runs, using each type of charcoal. Duplicate samples were obtained at the beginning, middle, and end of each run. As shown in Table I, all three charcoals were efficient in fluorine removal. Since the fluorine concentrations in the reactor exhaust were too small for accurate analyses, it was concluded that under the conditions of the tests each type and mesh of charcoal was equally efficient for the removal of fluorine. However, the wood charcoal left a resinous material in the reactor outlet which would eventually plug the exhaust line. Examination of the exhaust line after the completion of nine runs revealed that a concentrated solution of HF and corrosion products had formed. This condition was caused by water (driven from the charcoal) absorbing hydrogen fluoride and possibly fluorine from the exhaust gases. Runs 10, 11, and 12 were made to determine to what extent this condition caused misleading sample results. To prevent interference between charcoals, the exhaust line was cleaned between runs. The results, shown in Table I, indicate that the deposits had a small effect on the fluorine concentration in the exhaust.

The 5 to 7 mesh (as received) Barnebey-Cheney Type CG-2 charcoal appears to be as efficient as the smaller 7 to 10 mesh charcoal. The Barnebey-Cheney charcoal left

Table I

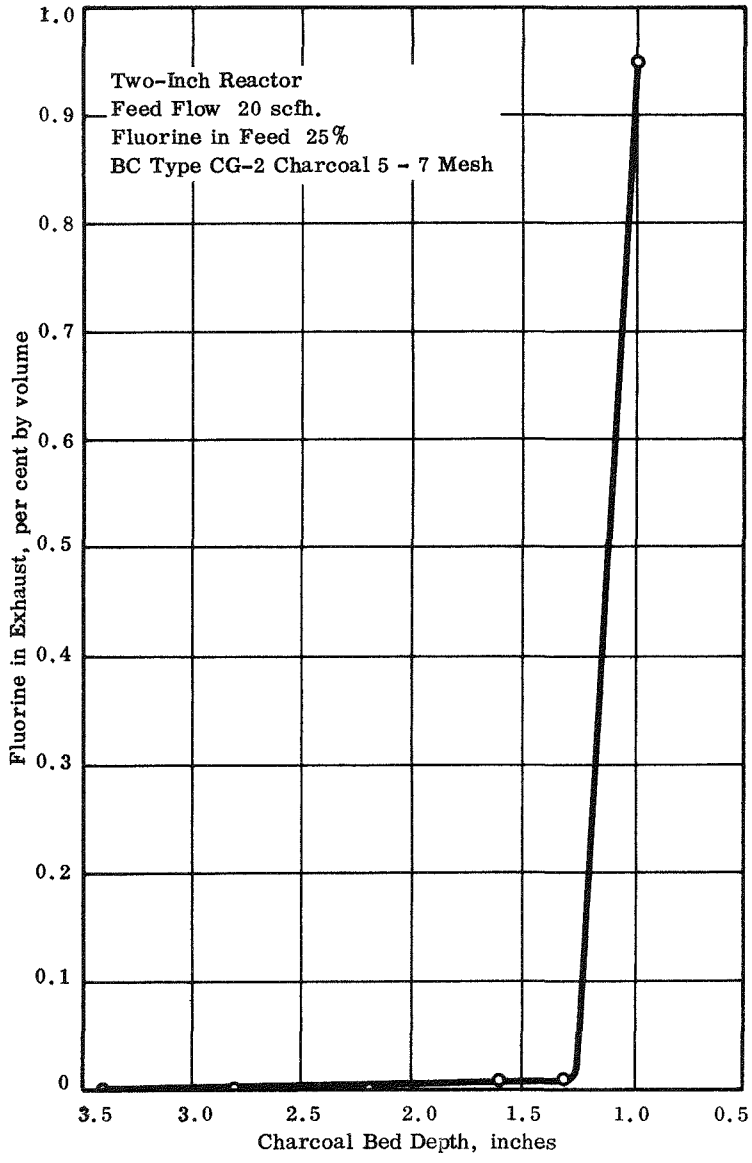
DATA FROM TWO-INCH REACTOR TESTS

Run	Charcoal*	Charcoal Bed Depth at Start, Inches	Total Feed Flow, scfh.	% F_2 In Feed	Reactor Exhaust Analysis		Maximum Reactor Wall Temperature, °F.
					% F_2	% HF	
1	PC – F	14.0	10	30	0.011	0.68	700
2	BC – F	14.0	10	45	0.0	0.52	940
3	PC – M	14.0	10	15	0.0	0.09	600
4	W – L	14.0	10	30	0.0	No Analysis	940
5	PC – L	14.0	10	45	0.0	No Analysis	970
6	BC – L	14.0	10	15	0.0	No Analysis	590
7	BC – M	14.0	10	30	0.0	0.10	860
8	W – M	14.0	10	45	0.0	0.13	980
9	W – F	14.0	10	15	0.0	0.50	650
10	BC – L	14.0	10	45	0.012	1.10	1000
11	PC – L	14.0	10	45	0.008	0.08	980
12	BC (5-7 Mesh)	14.0	10	45	0.0	0.73	1000
13	BC (5-7 Mesh)	2.5	10	25	0.03	0.37	680
14	BC (5-7 Mesh)	4.0	20	25	0.008	0.55	1020
15	BC-4815 (10 Mesh)	8.0	20	25	0.049	0.17	1200
16	BC-4816 (12 Mesh)	8.0	20	25	0.0	0.15	1180

*Definition of charcoal symbols:

BC = Barnebey-Cheney Type CG-2 (made from coconut shells)
PC = Pittsburgh Coke and Chemical Type BPL (made from coal)
W = Low grade wood charcoal

L = Large size (7 - 10 Mesh)
M = Medium size (12 - 16 Mesh)
F = Fine size (30 - 40 Mesh)



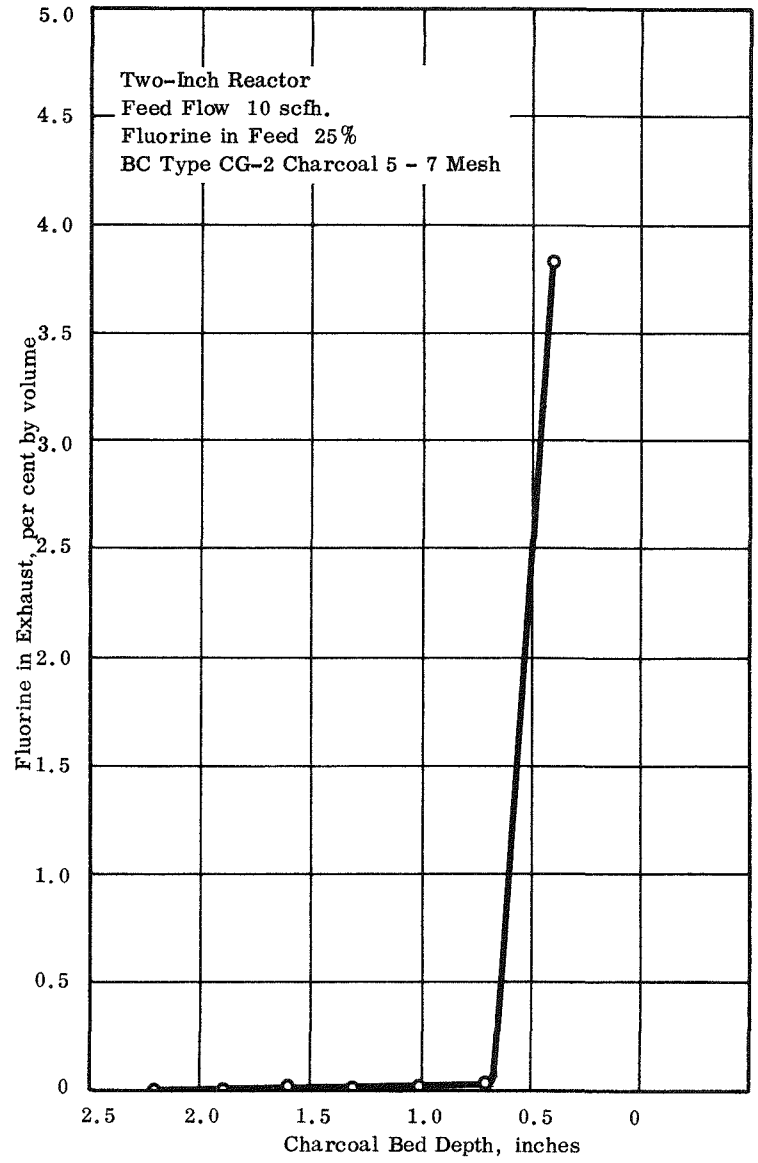


FIG. 5. CHARCOAL BED DEPTH VS FLUORINE CONCENTRATION IN EXHAUST

small deposits in the exhaust line, but the Pittsburgh Coke and Chemical charcoal left a considerable deposit of white material believed to be completely fluorinated volatiles driven from the charcoal.

Runs 13 and 14 were made to determine the effect of charcoal bed depth on fluorine removal. The bed depth was estimated from the amount of charcoal consumed during the run. The results, plotted in Figure 5, showed that a higher fluorine flow required a deeper bed for efficient removal of fluorine and that fluorine removal was very good until the bed became quite shallow.

Two additional Barnebey-Cheney charcoals were tested in Runs 15 and 16 (Table I). Both types were efficient for fluorine removal but left considerable deposition of reaction products in the exhaust line.

All five charcoals were equally efficient for fluorine disposal under the conditions of the test, but the Barnebey-Cheney Type CG-2 burned cleaner than the other charcoals tested.

FIVE-INCH REACTOR TESTS

The equipment for the 5-inch diameter reactor tests was basically the same as that used for the small reactor tests. However, a larger fluorine metering station and a larger nitrogen rotameter were installed, and the reactor exhaust was vented directly to the atmosphere instead of first passing through a chemical trap as in the small reactor tests.

All the runs were made using Barnebey-Cheney Type CG-2 charcoal (5 to 7 mesh) and 25 per cent fluorine in the feed stream at flows ranging from 100 to 400 scfh. as shown in Table II. Fluorine removal was very good for all flows with the fluorine concentration in the exhaust stream ranging from 0.03 per cent down to undetectable amounts. Very little odor of fluorine or HF could be detected in the vicinity of the exhaust.

Table II

DATA FROM FIVE-INCH REACTOR TESTS

(Barnebey-Cheney Type CG-2 charcoal and 25% fluorine in feed)

Total Feed Flow, scfh.	Maximum Reactor Wall Temperature, °F.	Reactor Exhaust Analysis		
		% F_2	% HF	% CF_4
100	1210	0.03	0.24	11.0
120	1340	0.00	0.33	-----
160	1420	trace	1.39	9.4
200	1560	0.02	1.14	8.6
250	1650	trace	1.04	11.7
300	1790	0.00	0.65	11.5
360	1665	0.00	0.32	-----
400	1540	0.01	0.35	11.1
300*	1750	0.03	0.07	11.3

*Relatively volatile-free charcoal.

The reactor wall temperature increased in proportion to the feed flow until the flow reached 300 scfh. when the wall temperature began to decrease (Figure 6). The higher flows of the feed gases caused the reaction to spread over a deeper zone, thus reducing the temperature at any one point. The time required for the reactor wall temperatures to reach near maximum is shown in Figure 7. Higher feed flow caused a more rapid temperature increase due to the larger fluorine input. The wall at the reaction zone was cherry-red at 1200°F. and became orange-red at about 1600°F. The reactor wall was attacked by fluorine as evidenced by a flakey scale of nickel and copper fluoride that had formed, but the corrosion did not appear to be extensive.

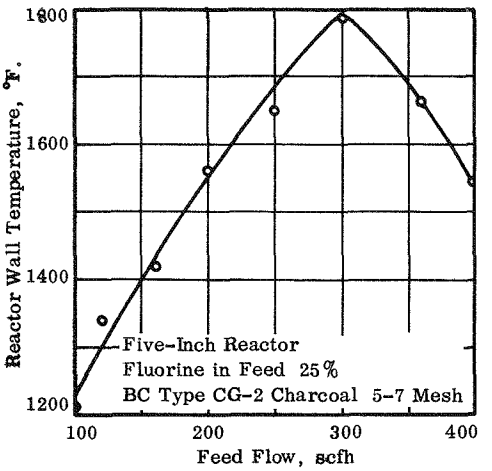


FIG. 6. REACTOR TEMPERATURE VS FEED FLOW

Figure 8 shows the variation of HF and CF_4 in the reactor exhaust with respect to the feed flow. Since the fluorine and HF concentrations in the feed were constant, any variation in HF concentration in the exhaust resulted from the reaction of fluorine with water or other volatiles in the charcoal. The HF concentration in the exhaust was consistently lower at the higher flows and temperatures. At the higher temperatures most of the volatiles were driven from the reaction zone before they could react with the fluorine to produce HF, thus allowing almost all the fluorine to react with carbon to form CF_4. It was assumed that the HF in the feed passed through the reactor unchanged.

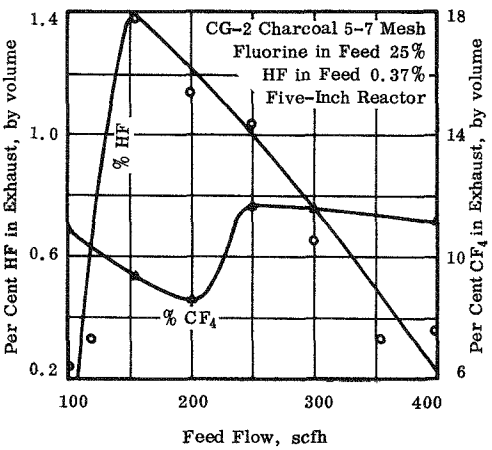


FIG. 8. FEED FLOW VS HF AND CF_4 CONCENTRATION IN EXHAUST

One run was made with charcoal which had been subjected to high temperatures during a previous run. The high temperature removed most of the water and other volatiles and, as expected, the HF concentration in the exhaust stream was significantly lower as shown in Table II.

Examination of the representative mass spectrum analyses of the exhaust gases of the small and large reactors (Table III) revealed more complete fluorination of the carbon to CF_4 in the larger reactor. This was due to the wider and deeper reaction zone which allowed longer contact time between the carbon and the fluorine at the high temperatures of the reaction zone. The reaction zone appeared to be about 4 inches deep at a feed flow of 400 scfh.

CONCLUSIONS

These tests indicated that fluorine could readily and efficiently be disposed of by reaction with charcoal. One gram of Barnebey-Cheney Type CG-2 charcoal consumed about 6 grams of fluorine. With a 5-inch diameter reactor and a feed flow of 400 scfh. (25 per cent fluorine) a 5-inch bed of charcoal would be consumed in about an hour. The reaction proceeded smoothly with no explosive tendency although the reactor wall became very hot at the reaction zone. A charcoal containing about 90 per cent free carbon should be used to avoid excessive reaction deposits in the reactor exhaust line.

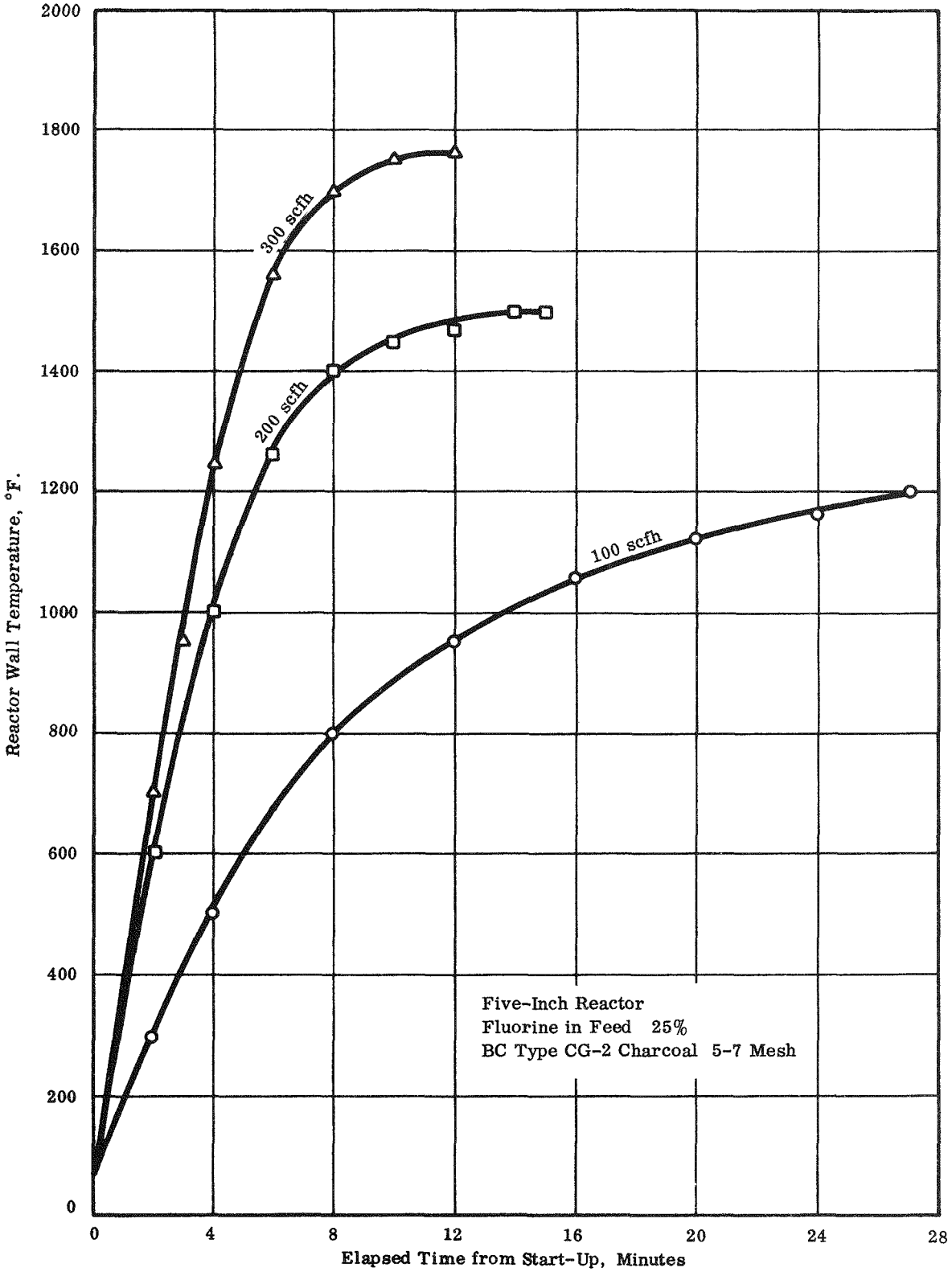


FIG. 7. REACTOR WALL TEMPERATURE INCREASE

Table III

MASS SPECTRUM ANALYSIS OF REACTOR EXHAUST

Ions or Compounds	Per Cent, by Volume	
	2-Inch Reactor	5-Inch Reactor
N_2	83.1	88.8
O_2	trace	----
A	trace	trace
HF	not shown	not shown
F_2	not shown	not shown
CO_2	0.1	trace
CF_4	12.9	11.1
C_2F_4	----	< 0.1
C_2F_6	2.2	< 0.1
C_3F_8	0.5	----
C_4F_8	0.1	----
C_4F_{10}	0.07	----
C_5F_{10}	0.04	trace

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