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DESIGN AND OPERATING CRITERIA FOR FLUORINE

DISPOSAL BY REACTION WITH CHARCOAL

By Harold W. Schmidt

Lewis Research Center
Cleveland, Ohio

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SUMMARY

Experiments with the charcoal-fluorine reaction for the disposal of fluorine have shown generally that this method is effective over a wide range of conditions. Pure fluorine or fluorine diluted with nitrogen to concentrations as low as 0.3 percent fluorine may be disposed of efficiently within the rate limitation. Maximum feed rates have been established and are inversely proportional to the charcoal-bed particle diameter. Moisture content in the charcoal had no appreciable effect on the disposal efficiency after the reaction zone was established and the moisture was driven off by the heat of reaction. There was no evidence of bed poisoning resulting from continued use.

Design parameters may be based on the stoichiometric requirements plus sufficient excess charcoal to maintain desired efficiency toward the end of a disposal operation. The length of time a given reactor may be used continuously is limited by the rate of fluorine input and the resistance of the system to heat and fluorine attack. Refractory-lined reactors have been in routine field use at the Lewis Research Center for over a year and have given satisfactory service over a wide range of conditions.

INTRODUCTION

The disposal of fluorine is often necessary upon shutdown of an operating system in order to remove unrecoverable or residual fluorine. In some operations, it may be necessary to dispose of larger quantities as an emergency procedure. The toxicity of fluorine makes direct venting to the atmosphere inadvisable in most locations, and a safe disposal facility generally is required.

The reaction of fluorine with an amorphous carbon, such as wood charcoal, has been reported (ref. 1) to be a feasible method for

disposing of gaseous fluorine according to the formula
$C + F_2 \rightarrow CF_4, C_2F_6, C_3F_8, C_4F_{10}, \ldots$. Charcoal acts as a fluorine-disposal agent by means of chemical reaction and not by adsorption. The gaseous fluorocarbons formed by this reaction are chemically inert and relatively nontoxic and may be vented directly to the atmosphere. Pure fluorine, fluorine-nitrogen, and fluorine-oxygen mixtures containing as little as 6.5 percent fluorine had been disposed of with resulting reactants containing less than 77.5 parts of fluorine per million of effluent.

For more efficient use of this disposal system, it is desirable to know its limitations and the extent to which the previously mentioned conditions can be varied or extended. The purpose of the present investigation was to supplement this information by determining:

(1) Minimum fluorine concentrations for spontaneous reaction and satisfactory disposal efficiency

(2) The fluorine feed-rate limitations

(3) The effect of charcoal-bed particle size

(4) The effects of absorbed moisture in the charcoal

(5) Bed-poisoning effects from continued use

(6) Possible design parameters.

A summary of the field operational use of this disposal method over a 12-month period is included.

APPARATUS AND PROCEDURE

Preliminary qualitative tests were made on a laboratory scale in Pyrex equipment for the purpose of observing the ignition and combustion characteristics of fluorine-nitrogen mixtures with carbon at low fluorine concentrations, and to determine the approximate concentration limits at which spontaneous reaction would occur.

Gas mixtures were prepared for these tests by means of the apparatus shown in figure 1. Mixtures were prepared batchwise by bypassing the rotameters and measuring the partial pressure and temperature of the mixture.

A small reactor, suitable for further evaluation of the fluorine-carbon reaction, was constructed using a horizontal through-put hopper configuration, as shown in figure 2. The burner size was kept small so that the maximum feed rates and dilution effects could be determined without excessive fluorine consumption.

The reactors used for initially evaluating this disposal method (ref. 1) and those actually being used in the field at the present time have been equipped with a top inlet feed so that the charcoal bed could support the hot combustion zone. The hopper design was chosen to test a possible alternate configuration as well as to maintain constant bed depth and volume throughout the tests, since designs other than the hopper configuration allow the charcoal bed depth to vary as the charcoal is consumed. The reactor was constructed of mild-steel sheet and lined with firebrick. A single copper inlet tube, 1/4 inch in diameter, served as the inlet nozzle; the product gases vented opposite to the inlet through one or more of four 1-inch vent lines.

Standard variety, crumbled charcoal was loaded through the removable top, which fit into an overlapping sleeve filled with sealing clay to provide a gas-tight seal.

Fluorine and fluorine-nitrogen mixtures were metered and fed to the burner with manually controlled Teflon-packed valves. Flow rates were measured with Teflon-packed glass rotameters equipped with aluminum floats and stainless-steel guide wires. Copper tubing (1/4 to 3/8 in.) and standard AN fittings were used for the rest of the system (fig. 2).

Quantitative measurements of the effluent from the hopper reactor were made to determine the amount of residual fluorine remaining in the reaction products. This was done by using an evacuated tank of known volume to draw samples of the effluent through potassium iodide solution. Residual fluorine was reacted out of the sample by the potassium iodide solution. A potassium iodide indicator paper was located downstream to insure 100 percent fluorine removal. The sampling system is shown in figure 3.

Free iodine released by the residual fluorine was acidified and titrated with a sodium thiosulfate - starch solution, and expressed in terms of grams of fluorine per cubic foot of effluent or in parts per million by weight. The average molecular weight of the reaction products was calculated from composition data reported in references 2 and 3. An average molecular weight of the carbon fluorides of 100 was used for these data. Although the actual molecular weight of the products may vary somewhat depending on the reaction rate and temperature of the products formed, the value was assumed to be constant for the conditions of these tests.

RESULTS

Fluorine Concentration

Table I summarizes the ignition and reaction characteristics of fluorine-nitrogen mixtures, as observed in the Pyrex equipment. Mixtures of 15 to 25 percent fluorine reacted spontaneously at the point of impingement, and with little or no time lag created a glowing reaction zone the same as that reported for pure fluorine (ref. 1).

The temperature of the reaction zone varied with the flow rate as indicated by the intensity of the radiation from the reaction zone; this varied from a dull red glow at very low flow to intense radiation at high flows.

At fluorine concentrations between 11 and 14.6 percent, the same results were obtained, except for a short time required for the reaction zone to reach an equilibrium temperature. During this lag time, white vapor or gas evolved, presumably steam and condensed fluorocarbons, indicating that spontaneous reaction had occurred. Each run was made with a fresh "cold" carbon bed. After the carbon bed had been heated from the initial run, the mixture could be impinged onto the hot charcoal with little or no time lag for equilibrium conditions. No attempt was made to measure this ignition delay because of the many controlling variables, such as fluorine concentration and temperature, flow rate, initial bed temperature and the charcoal-particle size.

Only a white vapor was evolved when a mixture of less than 10 percent fluorine in nitrogen was impinged into a cold charcoal bed and the chemical reaction appeared to continue although a combustion-type reaction, or "red coals", was not obtained.

The quantitative effect of fluorine dilution with inert gas on the residual fluorine content in the effluent is shown in figure 4. These data were obtained from the hopper reactor using an average charcoal particle size of 3/8-inch nominal diameter, with input concentrations of fluorine in nitrogen from 0.3 to 54 percent. The grams of fluorine per cubic foot of effluent for these low fluorine concentrations are compared with the average value for 100 percent fluorine and show no effect of dilution at feed rates up to 7 pounds per hour.

Flow Rate and Particle Size

The effect of flow rate on the residual fluorine in the reaction products is shown in figure 5. One curve was obtained using an average nominal charcoal-particle diameter of $1\frac{1}{2}$ inches, the other with particles with a $\frac{3}{8}$-inch average nominal diameter. The charcoal bed depth in both cases was approximately 11 inches. Flow rates were varied from 2 to 60 pounds per hour with 100-percent fluorine gas.

The maximum flow-rate limits of the 11-inch charcoal bed for the $\frac{3}{8}$- and $1\frac{1}{2}$-inch charcoal-particle size are indicated by the break in the curves. As the rate limit was exceeded, the disposal efficiency decreased rapidly.

The most significant effect shown in figure 5 is the difference in the maximum flow-rate limits resulting from the two charcoal particle sizes. Within the accuracy of the data, the ratio of the diameters is approximately equal to the ratio of the rate limits. This characteristic will be shown to be a useful design parameter.

Charcoal Moisture Content

Two sets of runs were made in order to evaluate the effect of water in the charcoal used for fluorine-burner-charge material. The first series of data were obtained using water-saturated charcoal (drained of excess water) from which the moisture content was allowed to diminish during the runs because of the heat of reaction. In the second series of runs, additional water was added to undrained charcoal so that the bottom of the burner contained about 1 inch of water in order to maintain saturation during the runs. In both cases, the extremely low fluorine content initially present in the effluent gases indicates an increased fluorine removal due to the scrubbing action of the water and the formation of hydrogen-fluoride.

After the reaction zone was established the residual fluorine in the effluent increased, but gradually returned to normal as the moisture was driven off by the heat of reaction (fig. 6). When the water content in the charcoal was maintained at saturation, the residual fluorine remained at a somewhat higher level than under normal, dry conditions. It would be reasonable to expect that at lower percentages of water content, the time required for equilibrium conditions would be much less.

Data for figures 4 to 6 are tabulated in table II.

Charcoal-Bed Poisoning

The quantitative data previously reported in reference 1 exhibited a slight but general increase in residual fluorine in the effluent from the beginning to the end of each series of runs, which suggested the possibility of charcoal-bed poisoning.

This effect was circumstantial, however, since in the present investigation the charcoal appeared equally effective after extended use as it did when fresh, and no evidence of bed poisoning was indicated.

Field Operation

In order to equip operation facilities with immediate disposal equipment utilizing the carbon-fluorine combustion method, a number of reactors were made using the top-inlet-feed system (ref. 1).

Standard ring-clamp-type 50-gallon drums were lined with 2 inches of castable refractory cement, with a 3-inch layer of the cement on the under side of the lids. The drum bottoms were not protected. The inlet tubes passed through the lid and ended flush on the inside at the refractory cement surface. A schematic diagram showing construction details is given in figure 7. Two or more of these drums connected in parallel have been used in preference to one large unit because the parallel-drum system provides continued disposal facility in the event of burnout in one of the units. Low fluorine flow rate through high-capacity reactors has on two occasions allowed excessive heating of the fluorine inlet nozzles in uncooled reactors, causing fluorine attack on the nozzles and refractory lining in the lid. Higher flow rates through the nozzles provided sufficient cooling to prevent this attack. The fluorine-disposal capacity per drum was approximately 100 pounds per hour, but in one test the equipment was operated at over 600 pounds per hour for approximately 3 minutes (equivalent to 30 lb fluorine) with a possibility of liquid fluorine entrainment, without damage to the reactor.

DISCUSSION

The reaction between charcoal and fluorine is similar to the common combustion of charcoal and air. It is unique only because of the high reactivity of fluorine, which provides spontaneous combustion.

As shown in figure 5, the maximum rate of fluorine disposal for an effluent containing less than 100 parts of fluorine per million of effluent was approximately four times greater for the 3/8-inch charcoal material than for the $1\frac{1}{2}$-inch material. Thus, the rate of fluorine disposal is inversely proportional to the nominal particle diameter. Since the ratio of the total external surface area per unit volume of charcoal is also 4 to 1 for the $\frac{3}{8}$- and $1\frac{1}{2}$-inch particles, this suggests that only the external surfaces of the charcoal particles are active in the reaction.

Therefore, the very large internal-surface area, which for porous material such as wood charcoal is many orders of magnitude greater than the external-surface area, contributes very little to the reaction.

A highly reactive material such as fluorine most likely reacts upon impact with the solid surface to form a product which is then desorbed from the surface. A high rate of desorption would be expected because of the large energy release accompanying the reaction. In this case, the controlling factor in the reaction-rate limit is the mass transfer by counter diffusion of the reactants and products into and away from the solid surface through the gas layer. At equilibrium reaction conditions, therefore, the rate limit would become proportional to the total active surface area. This may explain the small contribution made by the internal surface, since diffusion into and out of pores with large length-to-diameter ratios would be very much slower than diffusion to and away from the external surfaces.

The data show that the maximum disposal rate for optimum efficiency for the $1\frac{1}{2}$-inch charcoal particles was about 8 pounds per hour for the 0.18 cubic foot of effective charcoal volume; the limit for 3/8-inch charcoal particles was approximately 30 pounds per hour. Since the fluorine flow rate per unit volume of charcoal is inversely proportional to the particle diameter, then $R/V = K/D$ where

R fluorine flow rate, lb/hr

V charcoal volume, cu ft

D nominal charcoal particle diameter, in.

K proportionality constant

Using the maximum allowable rate values,

$$K_{(3/8\text{-in.})} = \frac{30 \text{ lb}}{\text{hr}} \times \frac{1}{0.18 \text{ cu ft}} \times \frac{3}{8} \text{ in.} = 62.5 \frac{(\text{lb})(\text{in.})}{(\text{cu ft})(\text{hr})}$$

and

$$K_{(1\frac{1}{2}\text{ in.})} = \frac{8 \text{ lb}}{\text{hr}} \times \frac{1}{0.18 \text{ cu ft}} \times \frac{3}{2} \text{ in.} = 66.6 \frac{(\text{lb})(\text{in.})}{(\text{cu ft})(\text{hr})}$$

Therefore, for engineering design approximations, an average maximum allowable disposal rate R may be expressed as

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

The volume term in the preceding equation represents the minimum requirements for maximum rate and does not allow for the fact that charcoal is consumed in the process. Therefore, additional volume is required equivalent to the volume of charcoal to be consumed. The stoichiometric charcoal requirement for fluorine consumption is 17.5 pounds of charcoal per 100 pounds of fluorine, based on the approximate product composition for carbon-fluorine reaction reported in references 2 and 3.

The length of time a given reactor may be used continuously is limited by the high temperature resistance of the reactor structure to fluorine attack, the heat capacity of the system, and the rate of fluorine input. The number of nozzles required for any given bed area are arbitrary; however, one to three nozzles per square foot have given satisfactory distribution.

The design criteria developed from the data obtained are based on the assumption that the reactor materials are capable of withstanding the operating conditions specified. Uncooled reactors of the type described previously have been used at rates up to six times their design capacity of 100 pounds per hour, for short periods of time without damage to the reactor. In order to have the simplification of an uncooled reactor, the best design practice would be to use two or more reactors whose total capacity was up to twice that required, depending on the total number of units.

Reactor-bed depth is arbitrary and may be subject to design convenience since the reaction is dependent on charcoal surface area, provided that the fluorine is impinged onto the charcoal surface and not into a nearby void space as could occur with a single layer of particles.

SUMMARY OF RESULTS

This investigation has shown generally that the carbon-fluorine disposal system may be operated effectively over a wide range of condi-conditions.

The following results were obtained:

1. 100 Percent fluorine or fluorine diluted with nitrogen to concentrations as low as 0.3 percent fluorine may be disposed of efficiently.

2. The maximum disposal rate R obtained for optimum efficiency was equivalent to

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

where D is the nominal charcoal particle diameter in inches and V is the reactor volume in cubic feet.

3. The maximum fluorine flow-rate capacity increases with a decrease in the charcoal-particle size, as shown in the preceding equation.

4. Moisture content as high as 30 percent in charcoal had no appreciable effect on reactor efficiency after the reaction zone was established and the moisture was driven off by the heat of reaction.

5. No evidence of charcoal-bed poisoning was indicated during this investigation.

6. 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.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, October 28, 1958

REFERENCES

1. Schmidt, Harold W.: Reaction of Fluorine with Carbon as a Means of Fluorine Disposal. NACA RM E57E02, 1957.

2. Ruff, Otto, and Bretschneider, Otto: Die Reaktionsprodukte der verschiedenen Kohlenstossformen mit Fluor II. Zs. f. Anorg. und Allgem. Chem., Bd. 217, Heft 1, Feb. 23, 1934, pp. 1-18.

3. Ruff, Otto, and Bretschneider, Otto: Die Zusammensetzung und Bildungswärme der aus Norit und aus SiC gebildeten Kohlenstossfluoridgemische. Zs. f. Anorg. und Allgem. Chem., Bd. 217, Heft 1, 1934, pp. 19-21.

TABLE I. - OBSERVED IGNITION AND REACTION CHARACTERISTICS OF FLUORINE-NITROGEN MIXTURES WITH CHARCOAL

Fluorine, percent	Remarks
25.4 22.0 20.6 18.9 18.9 18.3 16.9 15.95 15.5 15.0	Immediate ignition; red coals develop with little or no lag. Red reaction-zone temperature varies with flow rate; dull glow at very low flow; very bright at high flow.
14.6 13.5 13.4 11.6 11.1	White smoke evolved; red coals develop gradually. Reaction lag time decreased by increasing flow rate.
9.1 8.6 6.1 5.6	White smoke produced after some delay depending on flow rate.

TABLE II. - DATA FROM FLUORINE-DISPOSAL EXPERIMENTS

Fluorine in nitrogen, percent	Flow rate, lb/hr	Nominal charcoal particle diameter, in.	Moisture in charcoal, percent	Run time, min	Ratio of fluorine to effluent, $\frac{g \times 10^{-3}}{\text{std cu ft}}$ (a)	Fluorine in effluent, parts per million (a)
Effect of fluorine dilution with nitrogen						
54.4	<7	3/8	<6		2.4	30
50.0	----	---	----		2.5	29
31.4	----	---	----		2.1	31
22.2	----	---	----		.5	9
18.5	----	---	----		1.5	29
15.5	----	---	----		1.7	34
15.4	----	---	----		.9	17
14.0	----	---	----		4.9	98
10.0	----	---	----		4.8	105
2.5	----	---	----		4.2	111
.3	----	---	----		6.1	171
.3	----	---	----		4.9	137
Effect of flow rate and charcoal particle size						
100	2.1	3/8	<6		4.7	37
-----	2.4	---	----		5.1	41
-----	4.0	---	----		8.3	66
-----	4.0	---	----		4.1	32
-----	4.0	---	----		.8	6
-----	4.4	---	----		3.9	31
-----	4.5	---	----		2.5	20
-----	4.5	---	----		5.2	41
-----	9.0	---	----		2.1	16
-----	42.3	---	----		14.7	117
-----	61.0	---	----		31.2	247
Effect of flow rate and charcoal particle size						
100	2.2	$1\frac{1}{2}$	<6		12.1	96
-----	2.3	---	----		8.0	63
-----	4.0	---	----		8.5	67
-----	4.5	---	----		11.1	87
-----	8.0	---	----		5.5	43
-----	10.2	---	----		24.7	195
-----	48.4	---	----		104	825
Effect of moisture; saturation maintained						
100	<6	3/8	24	3.25	0.7	5
-----	----			5.25	2.9	23
-----	----			8.85	6.3	50
-----	----			10.25	17.7	140
-----	----			14.75	8.1	64
-----	----		29	18.45	9.0	71
Effect of moisture; high initial water allowed to diminish						
100	<6	3/8	30	2.0	1.72	14
-----	----	---		3.1	4.82	38
-----	----	---		5.0	4.4	35
-----	----	---		6.0	15.3	121
-----	----	---		8.0	10.9	86
-----	----	---		8.5	14.9	118
-----	----	---	19.8	11.0	2.9	23
-----	----	---	----	12.0	7.9	63
-----	----	---	----	18.2	3.8	30

[a]The parts per million of fluorine in effluent are not proportional to grams of fluorine ($\times 10^{-3}$) per standard cubic foot of effluent when dilute feed is used; nitrogen content in the effluent reduces the average molecular weight of a given sample volume thereby increasing the parts per million value whereas the grams per standard cubic foot are not affected.

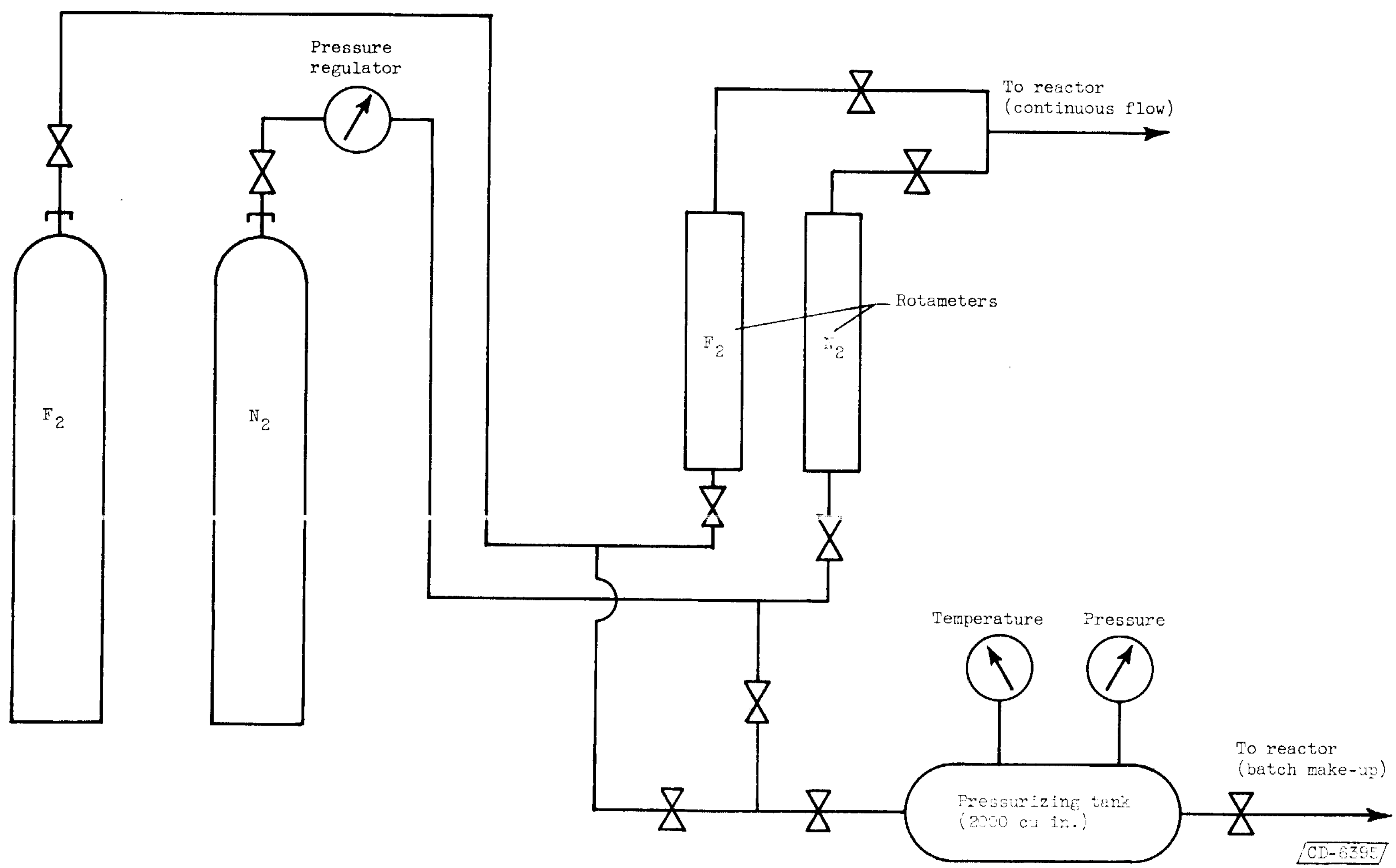

Figure 1. - Apparatus for supplying reactor feed at controlled rate and composition.

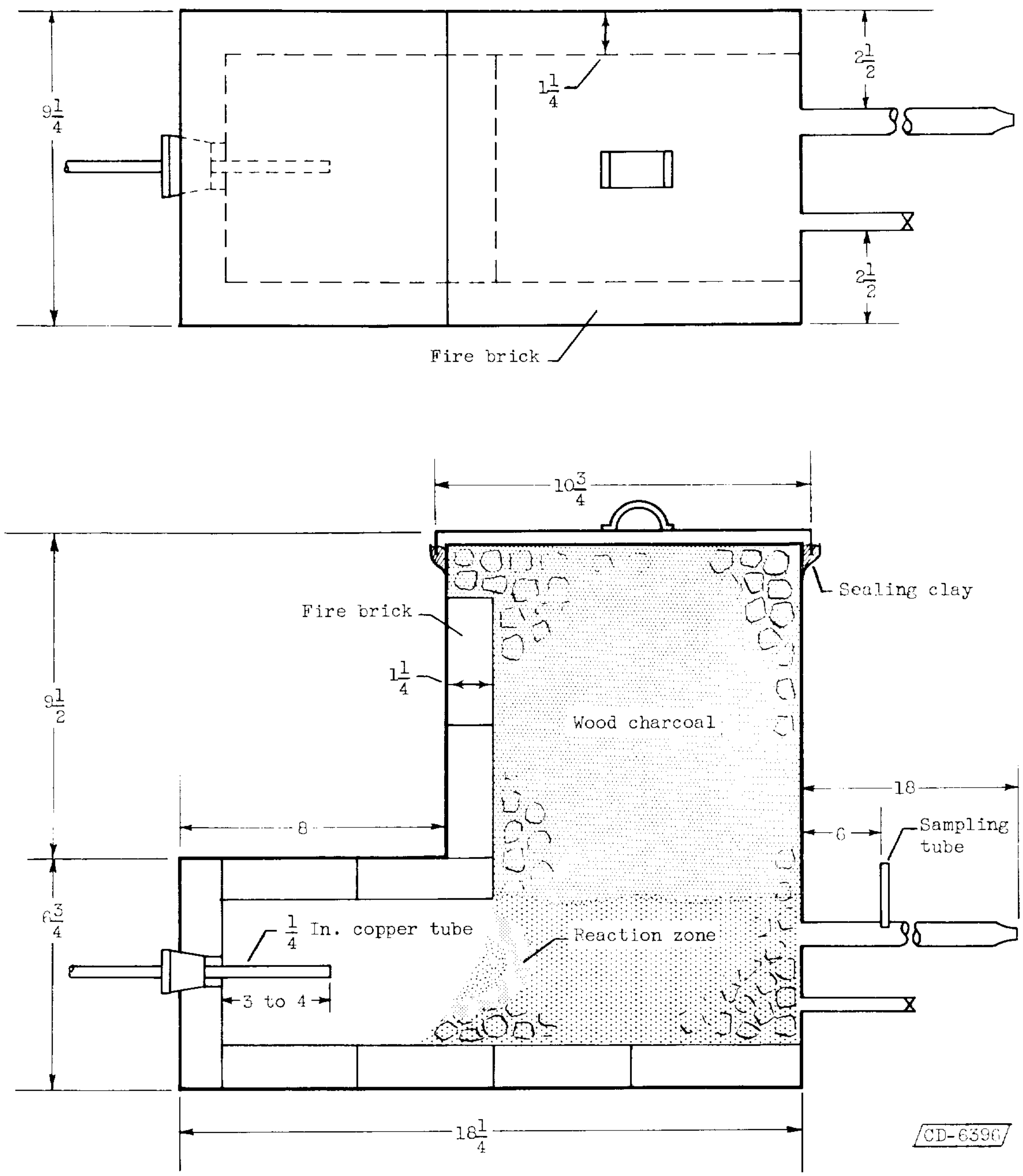

Figure 2. - Fluorine reactor. (All dimensions in inches.)

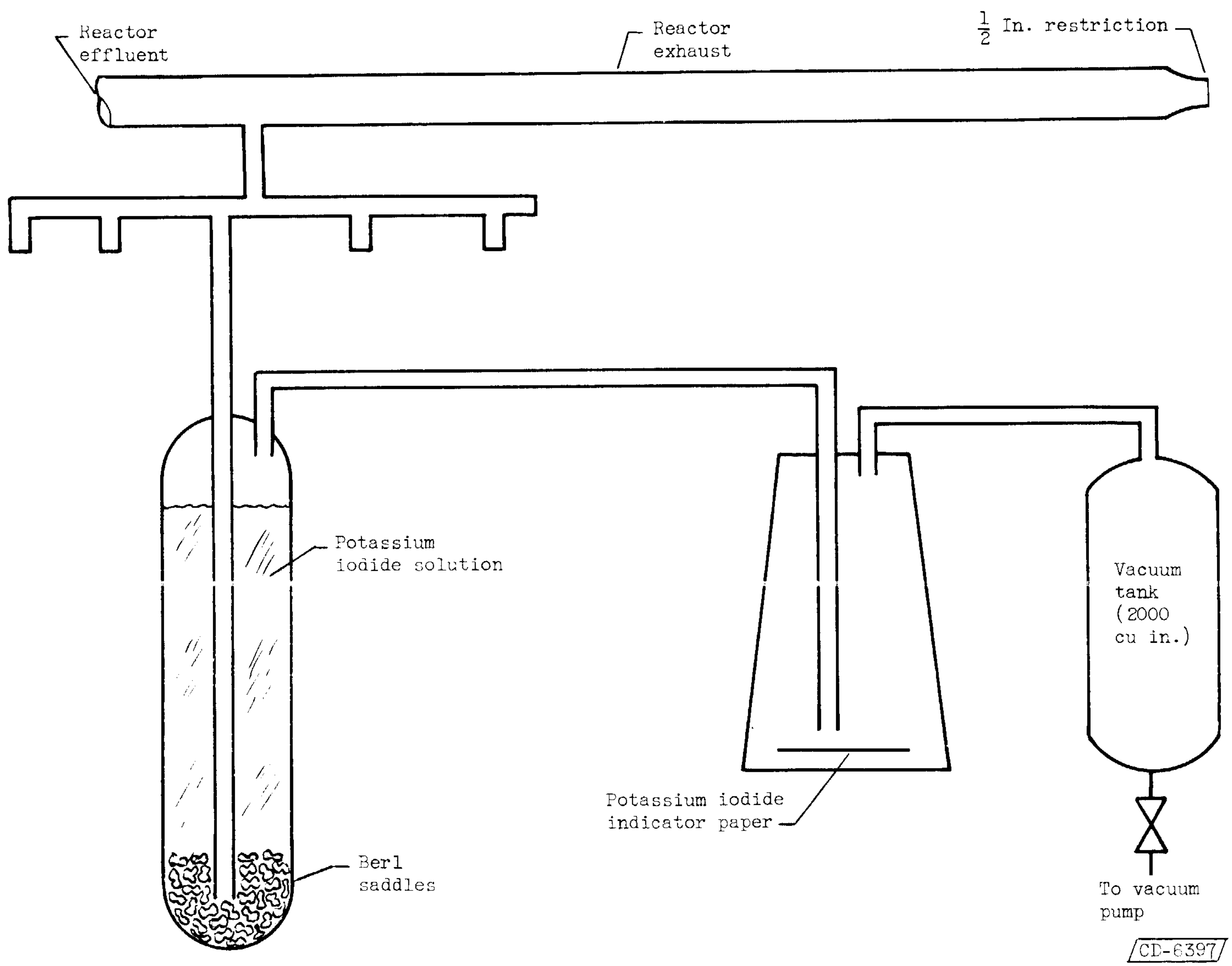

Figure 3. - Effluent gas-sampling system.

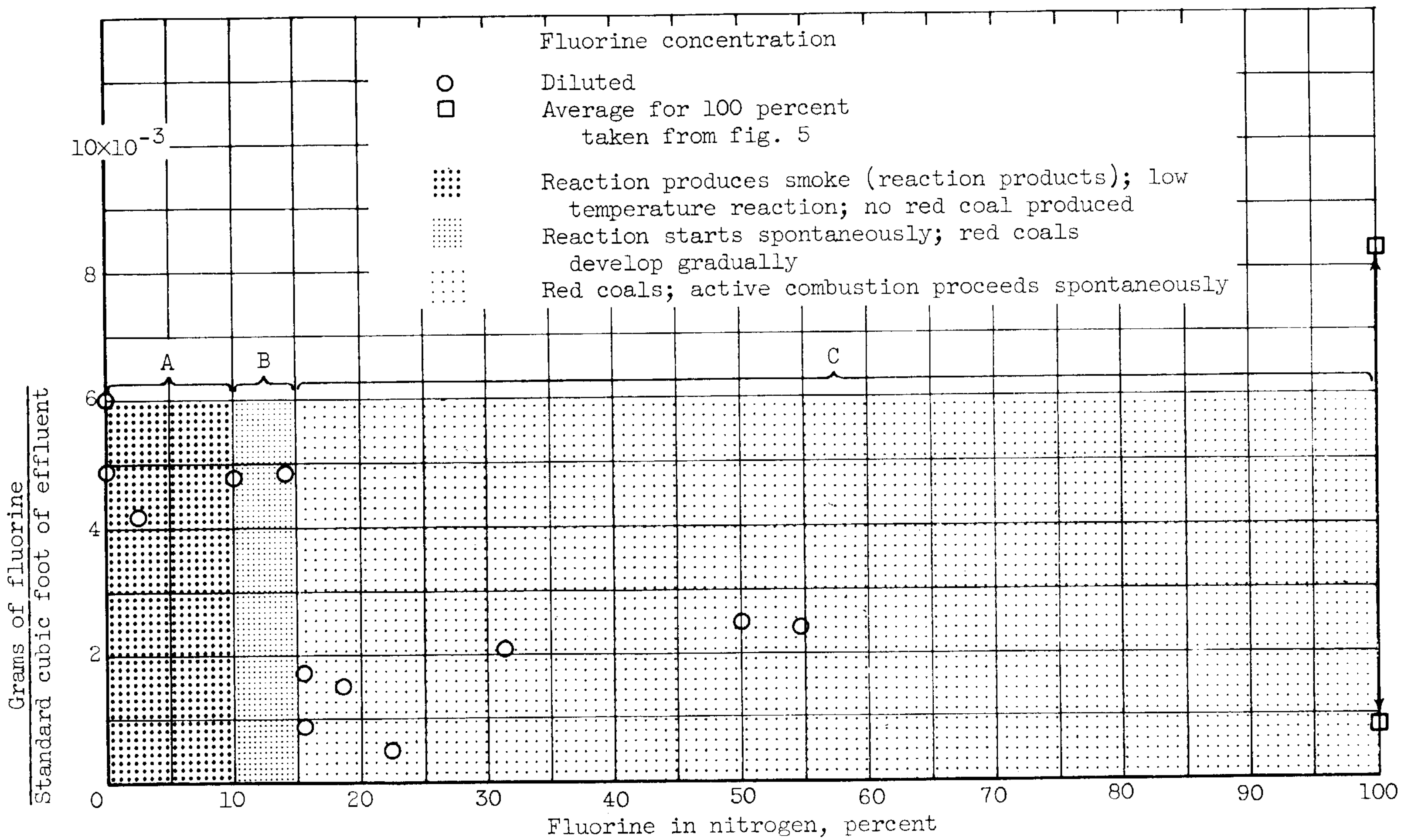

Figure 4. - Effect of fluorine dilution on disposal efficiency. Nominal charcoal-particle diameter, 3/8 inch; flow rate, 7 pounds per hour (maximum).

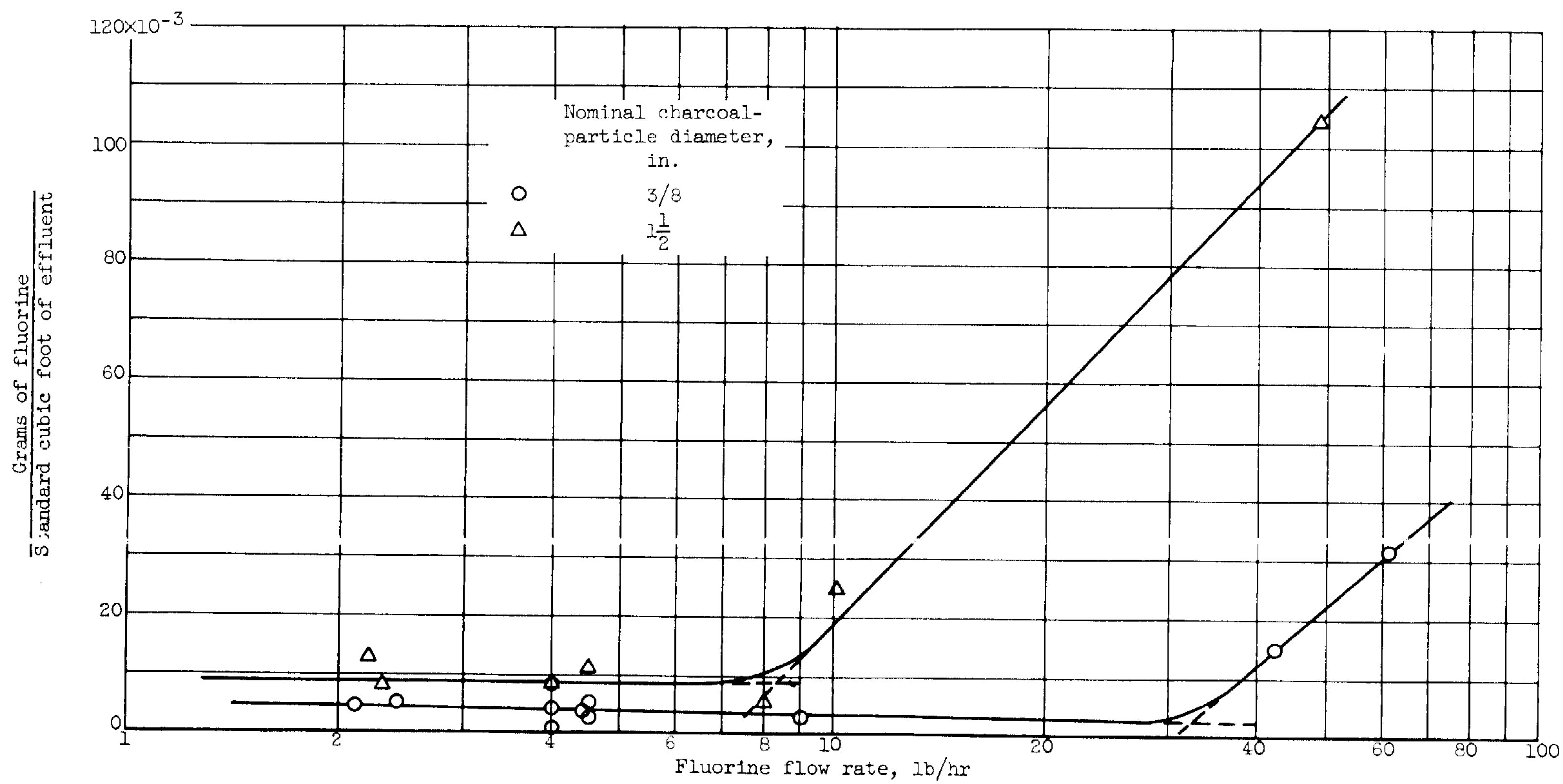

Figure 5. - Effect of feed rate and carbon-particle size on disposal efficiency. Charcoal-bed depth, 11 inches; effective cross-sectional area, 0.2 square feet.

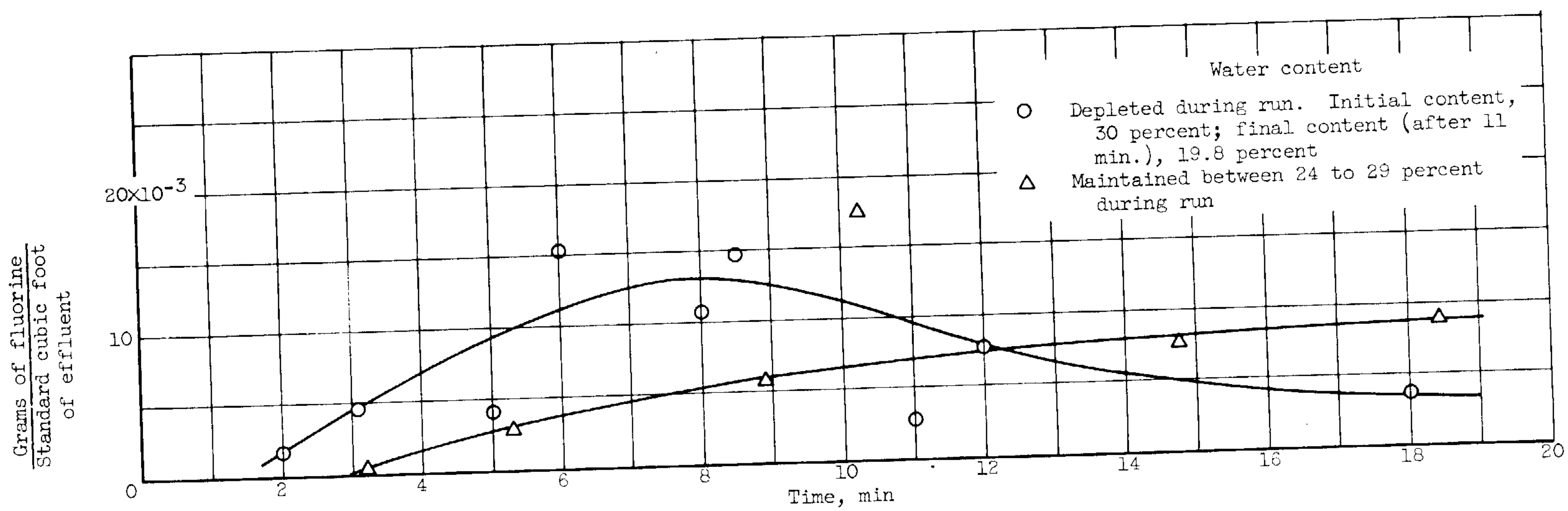

Figure 6. - Effect of water content in charcoal on the amount of fluorine in effluent

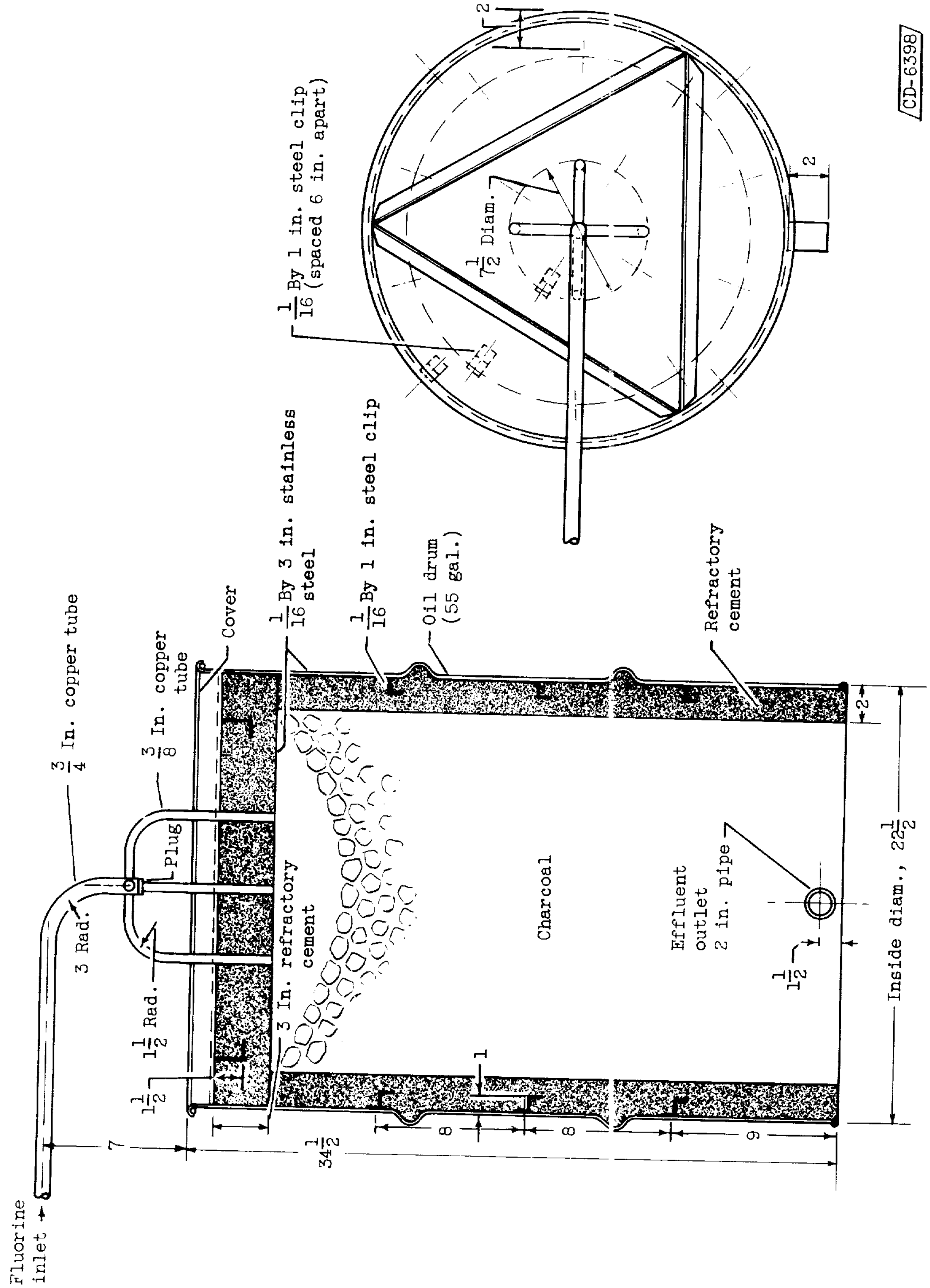

Figure 7. - Uncooled fluorine reactor. (All dimensions in inches.)