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Removal of Hydrofluoric Acid from Gas Streams by Solid Sorbents

C. H. Brown, Jr.
V. L. Fowler

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Chemical Technology Division

REMOVAL OF HYDROFLUORIC ACID FROM GAS STREAMS BY SOLID SORBENTS

C. H. Brown, Jr.
V. L. Fowler

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ABSTRACT

Removal of hydrofluoric acid (HF) vapor from gas streams via reaction with solid sorbents was investigated. The gas stream studied consisted of HF, steam, and nitrogen. The sorption process was studied in a bench-scale system using a plug-flow packed-bed reactor and the necessary ancillary equipment to deliver gas to the reactor and analyze the off-gas. Limestone and marble were eliminated as potential sorbents due to excessive calcium fluoride dust formation. Pebble quicklime (calcium oxide) was tested and found to be a very efficient scavenger for HF under controlled conditions. By first slaking the quicklime in situ the calcium utilization efficiency was measured to be 90%. The HF removal efficiency was also found to be very high, particularly during the first portion of a test when the HF concentration in the effluent was below the detection limit of the analysis method.

1. SUMMARY

Removal of hydrofluoric acid (HF) vapor from vent gas streams by reaction with a solid sorbent such as limestone was investigated as an alternative to wet scrubbing. This investigation was performed in a bench-scale system at Oak Ridge National Laboratory (ORNL) utilizing a 2.54-cm-diam tubular reactor, which was 152 cm tall. The reactor configuration studied was a packed bed with gas processed in the upflow mode. This was felt to be the simplest feasible system. A total of twelve experimental tests were performed with the system. Dolomitic limestone, marble chips, and calcium oxide (CaO or pebble quicklime) were studied as reactive solid sorbents.

Upon reaction with moist HF, both the dolomite and marble chips formed a large amount of fine particulate (<5 μm), which was entrained out of the reactor. These materials were not investigated further as potential sorbents for HF.

Most of the testing during this project was aimed at evaluating the third sorbent, quicklime. Under certain conditions it was found that quicklime will remove HF from moist gas streams with very high efficiency. The maximum HF loading measured in this test series was 0.63 g HF/g bed, which translates to a calcium utilization efficiency of 90%. This test was performed with 6x9-mesh calcium oxide that was slaked in situ prior to HF introduction. The test results indicate that the initial conversion to the hydroxide form is an important factor in obtaining high conversion of the available calcium to the fluoride form. The test data also indicate that it may be important to maintain the bed temperature below the temperature at which the hydroxide reverts to the oxide form.

The tests with quicklime indicate that a bed depth greater than 20 to 30 cm is not feasible with a 2.54-cm-diam reactor, due to wall friction effects that cause compaction and plugging of the bed. Tests with a staged reactor in which a series of five beds, each with a depth of 15 cm, could be operated satisfactorily with minimal solids binding in the bed. Solids particle size was found to decrease somewhat during reaction. The fines generated did not, however, tend to be transported out of the reactor.

2. INTRODUCTION

2.1 OBJECTIVE

Processes currently in use at several facilities result in excess HF that must be disposed of in an environmentally acceptable manner. A proposed method for accomplishing this is to react the excess HF with calcium, thus forming fluorspar (CaF_2), which can be disposed of easily. The thrust of the project that is reported herein is the bench-scale evaluation of the solid-phase calcium removal method with the following specific areas of interest:

1. demonstration of process feasibility with the particular streams of interest,
2. determination of process performance with respect to type and particle size of solid sorbent, temperature, and gas phase composition, and

3. recommendations of the best reactor configuration for actual use and further testing required at larger scale.

2.2 BACKGROUND

Several processes are currently in use for the control of fluoride emissions. The most prevalent are the wet scrubbing techniques. The HF is very soluble in water and reactive with alkaline materials. Advantage has been taken of both of these properties in past gas cleanup work. Scrubbing with water has been reported, wherein the generated aqueous fluoride is precipitated as calcium fluoride by the addition of lime, which can be removed from the scrubbing liquor by filtration.[1] A similar scrubbing process has been reported, wherein the process is improved by replacing the water by potassium hydroxide scrubbing liquid.[2] As in the water process, CaF_2 is precipitated by way of lime addition, then removed by filtration.

Previous work has also been performed to study the removal of HF from gas streams by static beds of limestone.[3-5] These studies indicated that the process was chemically feasible, although the studies were not conducted under conditions representative of the present study. One study indicated that excessive CaF_2 fines were generated when operating with oolitic limestone.[3] These problems were less severe when operating with nonoolitic material.

The present study investigated the use of limestone, marble, and quicklime as sorbent materials.

2.3 PROCESS OFF-GAS CHARACTERIZATION

The primary stream to be treated for HF removal emanates from the UO_2 conversion reactor, wherein UO_2 is converted to UF_4 in a batch fluidized bed reactor by contact with gaseous HF. The primary chemical reaction taking place in the conversion reactor is:

$$UO_2 + 4HF = UF_4 + 2H_2O \ . \qquad (1)$$

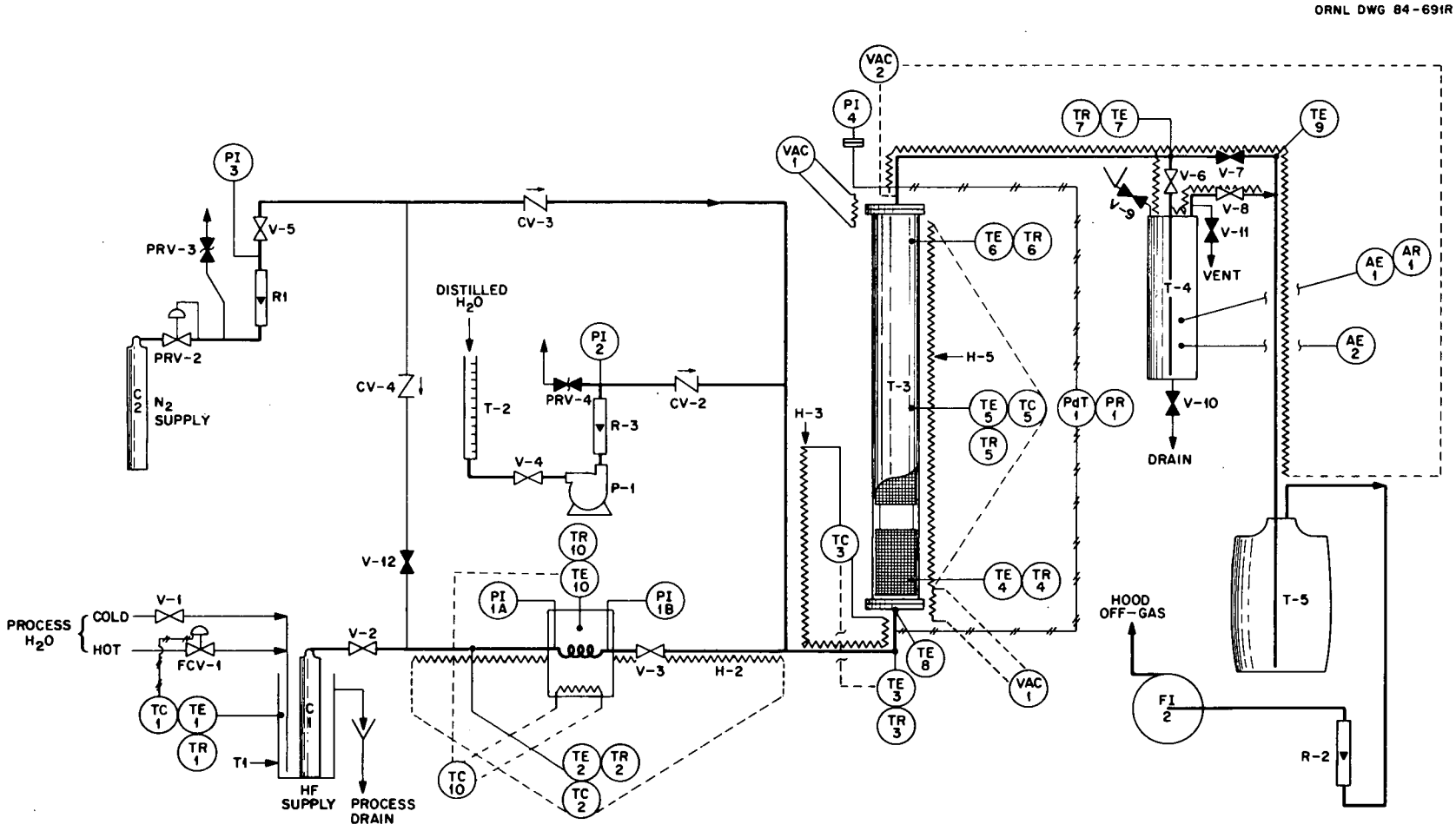
This reaction is exothermic, necessitating temperature control of the reaction mass, which is accomplished by the introduction of nitrogen gas. During the reactor cooldown portion of the cycle, HF flow is ceased. Since the reactor is operated in the batch mode and temperature is controlled by cycling the HF and N_2 flows, the effluent gas composition varies significantly during one reaction cycle. At the start of a cycle the effluent consists of N_2 and H_2O, whereas at the end of a cycle the effluent will be mainly N_2 and HF. By assuming that; (1) the N_2 flow is constant and sufficient to maintain minimum fluidization of the bed, (2) the initial reactor charge is 40 kg of UO_2, (3) 45 kg of HF is fed per cycle, and (4) HF is fed over a 4 h period, the following was arrived at as being representative of an "average" off-gas composition: N_2, 40 vol %; HF, 50 vol %; and H_2O, 10 vol %.

Most of the experiments were conducted with an off-gas composition (i.e., feed to the sorption reactor) near these values.

3. EXPERIMENTAL

3.1 APPARATUS AND PROCEDURE

The equipment used for the HF sorption studies is presented schematically in Fig. 1. The reaction vessel (T-3) was fabricated from a 1.5-m (5-ft) length of 2.54-cm (1-in.)-diam sched 40 Monel pipe. The reactor inlet and outlet were covered with 100-mesh Monel screen and in the initial phases of experimentation, charges of limestone and quicklime were loaded into the reactor to a depth of 1.1 m (3.75 ft) with the bottom screen serving as a bed support. Difficulties with discharging the reacted materials led to the use of a "Basket Train" insert. This insert consisted of five 14 x 14 mesh Monel screen baskets, 2.2-cm (7/8-in.) OD x 15.2-cm (6-in.) long, spaced 17.8 cm (7 in.) apart using 0.16-cm (1/16-in.)-diam Monel wire (2 ea., 180° apart) axially as stringers. Heat for the reactor was supplied by coiling 7.3 m (24 ft) of 18 ga. asbestos-coated nichrome wire (1300 W at 120 V) around the pipe. Reactor temperature control was provided by a voltage regulated on-off controller. The voltage was adjusted to that required to maintain a designated bed temperature (nominally 150°C in these studies). The controller was set at 500°C, thus acting as an overheat safety switch. This method permits observation of the reaction thermal effects independent of controller action.



HF SORPTION SYSTEM

Fig. 1. HF sorption experiment flow diagram.

Nitrogen was metered to the system through a calibrated rotameter. Similarly, water was metered to the unit by a variable speed peristaltic pump that was coupled to a rotameter. The preheater consisted of a 1.2-m (4-ft) length of 0.64-cm-OD (0.25-in.) Monel tubing wrapped with heating tape and insulated with fiberglass tape. The gas exit temperature is controlled by a voltage regulated on-off controller.

Anhydrous HF is delivered from a 1.9 m^3 (67.5 ft^3) cylinder that is immersed in a controlled temperature hot water bath. The hot water temperature sets the HF delivery pressure. The HF is metered to the preheater via a calibrated capillary tubing (0.381-mm-ID x 15.2-cm-long) flowmeter that is housed inside a standard laboratory furnace maintained at 110°C. A needle valve is used to control the HF flow rate. The HF mass flow rate is proportional to the difference between the square of the absolute pressures upstream and downstream of the capillary. Heating tape with variable voltage control was used on exposed lines to maintain temperatures >100°C.

The reactor effluent was directed through an analytical vessel (T-4) and/or a potassium hydroxide scrubber (T-5) via heat-traced Monel tubing. The analytical vessel was fabricated from PVC pipe, 10-cm (4-in.)-OD sched 40 x 38-cm (15-in.) long, and equipped with pH and fluoride ion electrodes. Scrubbing solution within T-4 was a 2.0-L volume of total ionic strength adjusting buffer (TISAB). The TISAB was used as a scrubbing medium to permit semicontinuous measurement of fluoride concentration in the reactor off-gas. The

fluoride-specific ion electrode method required that the solution pH be in the range of 5 to 7 and that the total ionic strength be relatively constant. Under these conditions the millivolt signal can be related directly to aqueous fluoride concentration. The efficiency of the TISAB as an HF scrubbing medium was tested and found to be nearly quantitative in the pH range of 5 to 7. The T-5 scrubber is a 22.7-L (6-gal) vessel containing 5.0 M KOH solution. The scrubbed effluent is metered through a Monel wet test meter.

A typical sorption test is described below. Each of the five baskets was charged with 50 g of solid sorbent, and the loaded assembly was placed in the reactor. After leak-testing all fittings, nitrogen flow at the rate of 0.6 L/min was initiated through the reactor. The effluent flowed directly to T-5. Heaters on the system were then activated and controllers set to produce the desired temperatures; reactor bed at 150°C, feed gas preheater at 140°C, all line heaters at ~110°C, and the HF station at 110°C. The hot water bath for the HF cylinder was brought to 55°C, which produced a cylinder pressure of 207 kPa (30 psi). While awaiting temperature stabilization, the fluoride electrode and pH meter were standardized. The T-4 vessel was charged with 2 L of TISAB. When all temperatures were stable, distilled water at the rate of 1 g/min (1.23 L/min vapor) was metered to the preheater. After allowing the system to stabilize, HF flow was initiated at the rate of 0.6 g/min (0.67 L/min gas). The resulting feed gas to the reactor contained 22.8 vol % N_2, 50.0 vol % H_2O, and 27.2 vol % HF. The fluoride ion concentration was continuously monitored by passing the reactor effluent through the analytical vessel. The buffering solution was replenished as required. The test continued until feed

and effluent concentrations were equal. At that point, the HF feed supply was discontinued, as was the water flow. All heat to the system was also deactivated. A N_2 purge was maintained during cool-down. The HF cylinder was weighed before and after the test to verify the accuracy of the HF metering capillary. After dismantling the reactor, the bed material from each of the five baskets was weighed for net gain determination, and samples of each were analyzed for calcium and fluorine content.

3.2 DISCUSSION OF RESULTS

A summary of operating conditions for the nine tests performed is given in Table 1. Tests 1 and 2, performed with dolomite and marble, respectively, produced similar results; fine particles of CaF_2 (<5-μm diam) were formed that were transported out of the reactor and subsequently plugged the reactor effluent lines and associated valving. Since production of CaF_2 fines is a problem that makes the system unattractive for scaleup, no further tests were made using limestone or marble. All subsequent tests were performed utilizing calcium oxide as the solid phase.

A chemical analysis of the calcium oxide used (obtained from Tenn-Luttrell Lime Co.) in tests 3-12 is given in Table 2, which indicates the material to be very nearly pure CaO with trace quantities of Mg, Si, and F present. The gas phase fed to this system consisted of water, HF, and nitrogen (as a diluent). The major potential chemical reactions are:

$$CaO + H_2O = Ca(OH)_2, \qquad (2)$$

Table 1. Summary of operating conditions for HF sorption tests

Test No.	Solid phase	Particle size[b]	Solid charge[c] (g)	Bed depth (cm)	Initial temperature[d] (°C)	Maximum bed temperature (°C)	Feed analysis[a]				Comments
							Flow rate (std L/min)	Composition (vol %)			
								N_2	HF	H_2O	
1	Dolomite	9 x 60	850.5	114.3	300		2.6	40	51	9	Severe dusting and plugging downstream of reactor by CaF_2 particles <5 μm diam
2	Marble	9 x 32	716.2	114.3	300		2.6	40	51	9	Severe dusting and plugging downstream of reactor by CaF_2 particles <5 μm diam
3	Pebble quicklime	<1.27 cm	484.0	114.3	300	>700	1.74-2.63[e]	40-60	26-51	9-14	1 h operation followed by rapid reactor plugging, no dust formation, noted high heat of reaction, lower 6-7 in. of reactor plugged, rest free-flowing
4	Pebble quicklime	6 x 9	471.5	114.3	145	270	1.9	55	30	15	2 h operation followed by rapid reactor plugging, no dust in off-gas, HF <150 ppmv in off-gas, bottom 1 ft and top 1.5 ft of bed free-flowing, mid-zone packed solid
5	Pebble quicklime	1.27 x .95 cm	459.4	114.3	135	277	1.9	55	30	15	2.5 h operation, aborted run when ΔP = 52 in H_2O, noted bed conditions identical to test 4
6	Pebble quicklime	1.27 x .95 cm	72.0	17.8	200	340	1.9	55	30	15	Short bed test, operated until HF breakthrough, $\Delta P \leq 1$ in H_2O, bed easily removed from reactor, 20 min operation with no HF in off-gas
7[f]	Pebble quicklime	1.27 x .95 cm	171.0	76.2	160	271	1.9	55	30	15	First test with 5 basket (copper screen) reactor insert, system operated until complete HF breakthrough obtained, $\Delta P \leq 1$ in H_2O entire test, complete HF removal first 50 min, product solids easily removed from baskets
8[f]	Pebble quicklime	6 x 9	226.7	76.2	185	265	1.9	55	30	15	System operated without problem other than reaction of HF with lower 2 copper baskets
9[g]	Pebble quicklime	6 x 9	244.6	73.7	205	290	1.9	55	30	15	First test with 5 basket (Monel screen) reactor insert. Complete HF removal for 220 min, CaF_2 easily removed from baskets
10	Pebble quicklime	6 x 9	246.5	74.2	215	433	2.1	48.4	40.4	11.2	Test at elevated HF concentration and temperature. HF metering capillary partially restricted
11	Pebble quicklime	6 x 9	241.8	72.8	180	440	2.4	45.9	43.2	10.9	Rerun of Test 10
12	Pebble quicklime	6 x 9	243.5	73.3	180[h]	350/315[i]	2.6	22.9	28.1	49.0	Initial conversion of CaO to $Ca(OH)_2$ followed by HF sorption

[a]Nominal values during test.
[b]Standard screen size except where noted.
[c]Initial mass of solid phase charged to reactor.
[d]Nominal value at bed center.
[e]Variations are due to changes in HF flow rate to control temperature.
[f]Test performed with copper screen basket reactor (5 baskets each 6 in. high).
[g]Test performed with Monel screen basket reactor (5 baskets each 6 in. high).
[h]Before H_2O introduction and before H_2O + HF initiated.
[i]Maximum during: hydration/HF reaction.

Table 2. Chemical characterization of calcium oxide feed material

Constituent	Concentration[a] (wt %)
Ca	69.84
Mg	0.46
Si	0.62
F	0.13
O[b]	28.95

[a]Normalized value based on calculated oxygen content.

[b]Calculated by mass balance.

$$Ca(OH)_2 + 2HF = CaF_2 + 2H_2O, \quad (3)$$

and

$$CaO + 2HF = CaF_2 + H_2O. \quad (4)$$

Equations 2-4 indicate two reaction pathways from CaO to CaF_2, dependent on whether or not water is present in the gas stream. The end product with the presence of water is a mixture of CaO, $Ca(OH)_2$, and CaF_2, the exact mix of which depends on relative abundance of HF and H_2O in the feed gas and the extent of reaction in the solid phase. In any event, the end product of reaction of the solid with HF is CaF_2.

The first three tests (Nos. 3-5) with CaO ended with similar results, a plugged reactor. Test 3 was performed with "as received" CaO, consisting of particles sized to 100% less than 1.27-cm diam, which included a large fraction of fine material. Tests 4 and 5 were performed using CaO sized to 6 x 9 mesh and 1.27-cm-diam x 0.95-cm-diam, respectively. In test 3 the blockage occurred in the lower 15 to 18 cm of the reactor, with the upper zone being free flowing. In tests 4 and 5 the lower 31 cm and upper 46 cm of bed were free flowing, and the middle zone (37 cm) was packed solid.

A possible explanation for this phenomenon follows. In a tubular reactor packed with solids there exists a critical length-to-diameter ratio (L/D). If the critical L/D is exceeded, a condition exists that prevents movement of the solids mass relative to the reactor walls. This phenomenon is mainly due to friction forces that develop between the bed mass and the reactor wall and interparticle bonding caused by chemical reaction. In practice, many systems exhibit a critical L/D

of approximately 8.* The absolute value is a function of bed and reactor material, packing density, solid particle size, and particle size distribution.

The molar volume of the bed material can increase significantly during hydrofluorination (CaO = 17 cm^3/mol, and CaF_2 = 25 cm^3/mol). If the height of the mass transfer wave front exceeds the critical L/D, then as the reaction mass tries to expand the solids will bind and compact, thus causing plugging of the reactor. It is also probable that the effect of factors such as packing density and extent of hydration has a significant impact on the plugging location and the allowable L/D in this particular system.

To test the operability of a short bed, test 6 was performed utilizing an 18-cm-deep bed (critical L/D for the reactor is ~ 20 cm). As noted in Table 2, this test was performed without any difficulty and with no indication of plugging or fines carryover. The results from test 6 indicated that a bed ~18 cm tall could be operated successfully. To increase the bed depth available for reaction to >18 cm, a basket insert as is described in the previous section was fabricated to fit the reactor. Tests 7 and 8 were performed with the first insert, which was fabricated from copper screen. Test 7 was made with 1.27 cm x 0.95 cm CaO, and test 8 was performed with 6 x 9 mesh CaO, while both tests were performed without signs of reactor plugging or fines carryover. During test 8 there were indications that HF was reacting with the copper basket material. For this reason, a new basket assembly was built from Monel screen, with dimensions identical to the copper assembly. Tests 9 - 12 were

*J. F. Fisher, personal communication, ORNL (1984).

performed using this assembly; test 9 was made using the 6 x 9 mesh CaO, without any problem.

Tests 10 - 12 were all made using the 6 x 9 mesh CaO material. Test 10 was intended to be a test at elevated HF concentration (40% vs 30%) and, therefore, temperature. During the test, the HF metering capillary became plugged, thus clouding data interpretation. Test 11 was made as a repeat of test 10, while test 12 was made at elevated H_2O concentration (49% vs 15%). Prior to HF introduction in test 12, water was fed to the system until the CaO bed was completely converted to $Ca(OH)_2$. Tests 10, 11, and 12 were performed without indication of reactor plugging, fines carryover, or other bed mechanical difficulties.

An example of the raw data taken during a test is depicted in Figure 2, where HF mass flow rate is plotted as a function of elapsed time during test 12. A separate curve is given for feed and effluent data. The data points for the feed flow rate were obtained from the capillary mass flowmeter. Two straight lines are shown; one for the average feed flow rate via the capillary, and one representing the average flow rate obtained from HF cylinder mass balance. The two differ by ~4%. The effluent concentration data were obtained by interpretation of the fluoride ion electrode signal, which is proportional to the fluoride concentration in the scrubber liquid. Initial breakthrough occurred at 100 min, indicating a wave velocity of ~0.75 cm/min.

The HF loading data are summarized in Fig. 3, where the normalized effluent concentration (ratio of effluent to influent HF concentration) is plotted as a function of HF mass loading for the various tests.

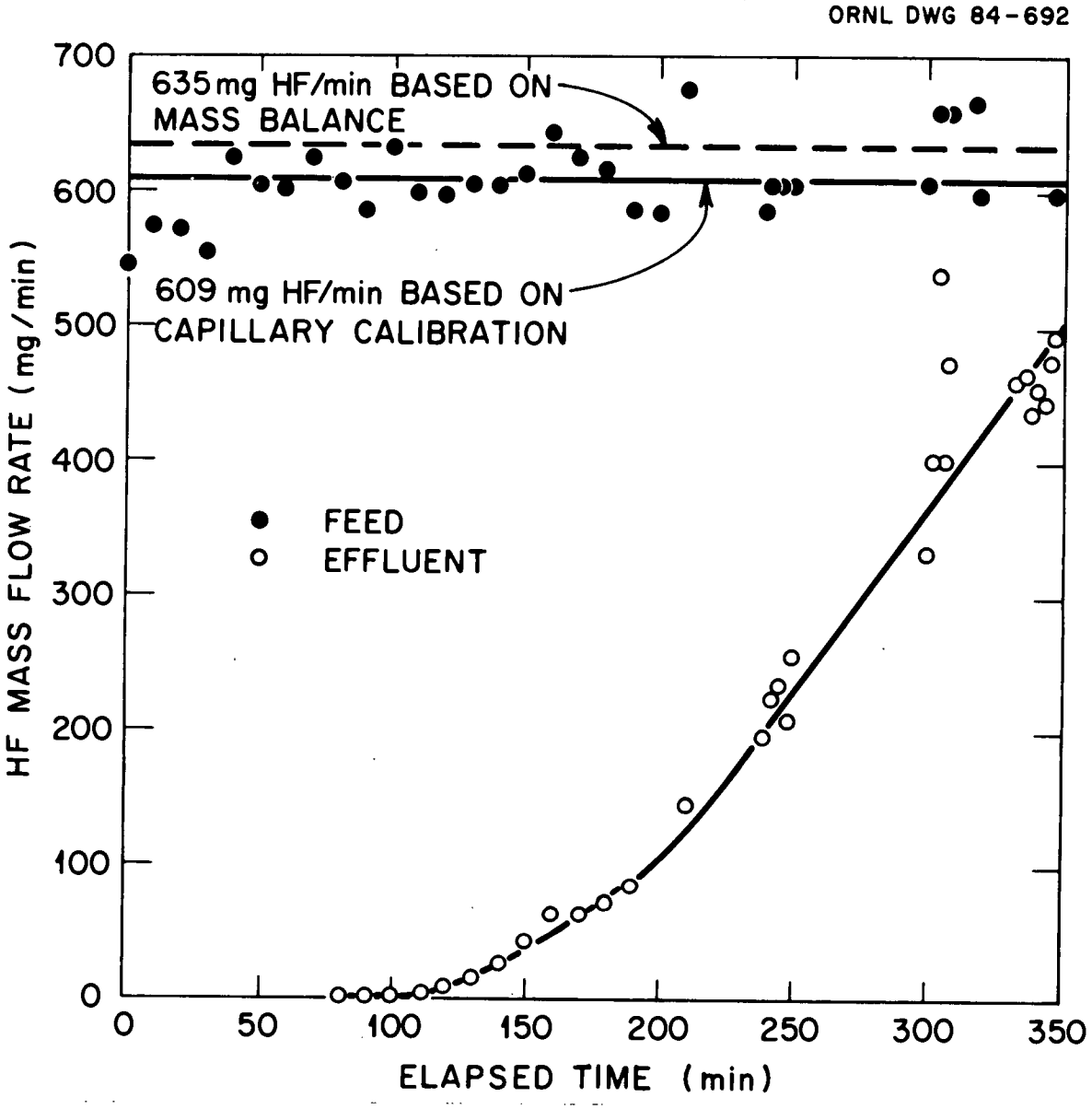


Fig. 2. Feed and effluent HF mass flow rate measured during test 12 presented as a function of time.

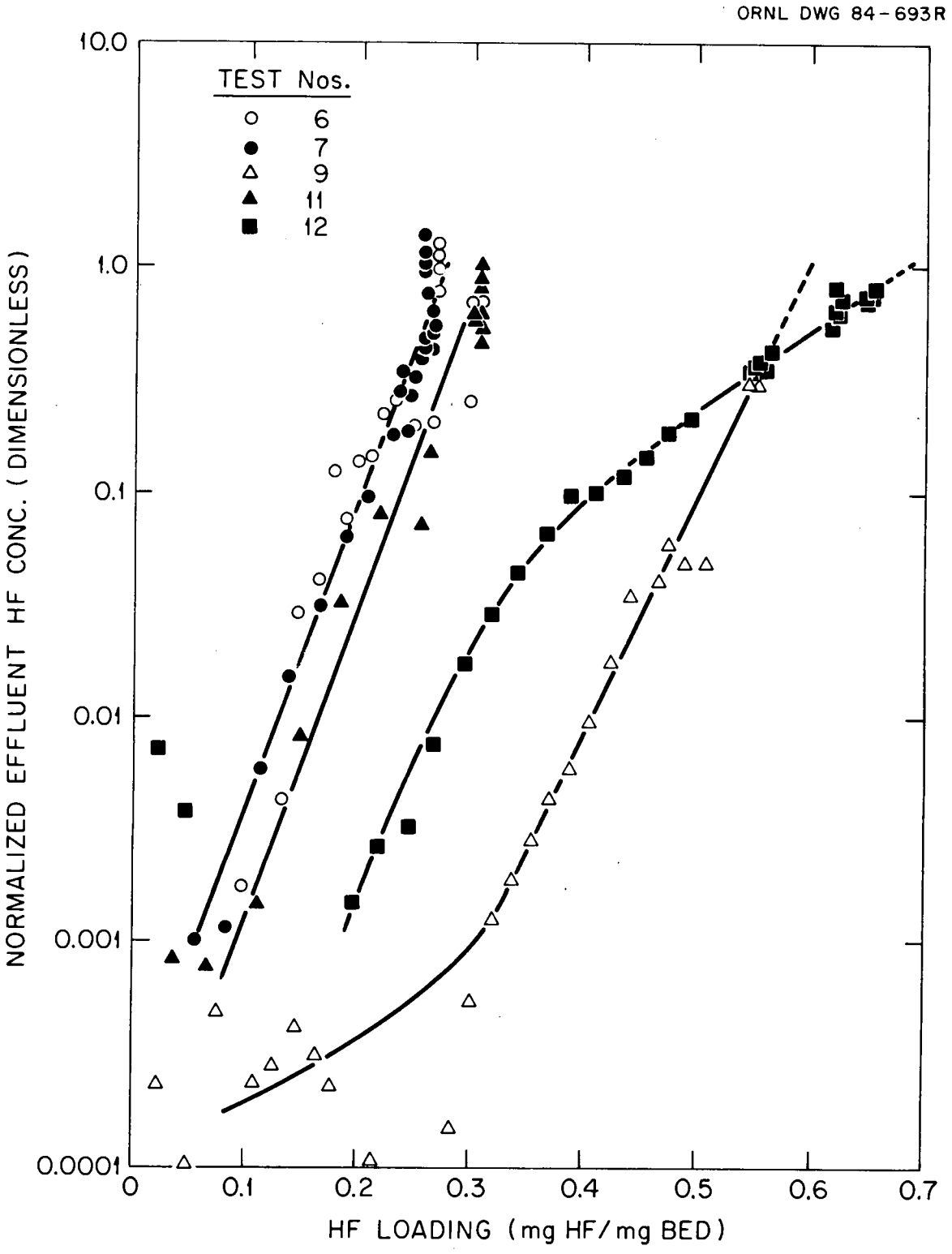


Fig. 3. HF mass loading data for calcium oxide bed material.

The maximum theoretical loading is 0.7 mg HF/mg bed, based on the amount of calcium in the feed. The data for tests 6 and 7 coincide, indicating that for a given loading the normalized effluent is the same, independent of bed mass. These data indicate a maximum capacity on the 1.27 cm x 0.95 cm material of 0.27 mg HF/mg bed, or 39% of saturation. The loading data for test 9 (6 x 9 mesh CaO) indicate a maximum loading of 0.6 mg/mg, or 86% of saturation. Comparing the test 6 and 7 data to the test 9 data indicates an increase in loading capacity of about a factor of two. The increased capacity is likely due to increased surface area rather than a decrease in diffusion resistance. A change in diffusion resistance would be indicated by a change in slope in the breakthrough curves for the various tests, which was not measured. Further testing would be required to elucidate the relative roles of mass transfer and chemical reaction in this system.

Test 11 was performed with the 6 x 9 mesh CaO at an elevated HF concentration (40% vs 30%) and, consequently, a higher bed temperature (440°C vs 300°C). As indicated in Fig. 3, the HF loading attained in Test 11 was 0.31 mg/mg, or ~50% of that obtained in test 9. It was felt that the decrease in capacity was a function of the state of hydration of the bed. The hydration reaction is given as Eq. (2), wherein CaO is converted to $Ca(OH)_2$ in the presence of water. The equilibrium in this reaction shifts to favor the dehydration reaction at ~400°C, thus forcing the hydrofluorination reaction to proceed via Eq. (4). As noted above, the bed temperature reached 440°C during the course of the experiment. To further investigate the hydration

effects, test 12 was performed. In this test, the CaO bed was completely hydrated before introduction of HF to the system. In addition, the HF concentration was lowered slightly to maintain the bed temperature at below 400°C. As shown in Fig. 3, the loading, extrapolated to saturation, was 0.68 mg/mg, or 97% of theoretical. It is felt that the hydration step is responsible for fracturing the CaO particles and increasing the available surface area for reaction. There was significant decrease in particle size due to the hydration/hydrofluorination reactions. A particle size analysis of the reacted product is presented in Table 3. As indicated by the data in Table 3, the average particle size after reaction was 1160 μm in diam as compared to 2654 μm in diam before reaction. The particle size distribution could have been affected somewhat by removal of the solids from the reaction baskets. There were no indications of particle transport out of the reactor during operation.

A summary of calcium conversion data, HF loading, and Ca and HF mass balance data is given in Table 4. The mass balance data indicate reasonable closure of both the calcium balance (-6% to +7%) and the HF balance (-6% to +11%).

4. RECOMMENDATIONS

The results from the bench-scale tests performed as part of this project indicate that dry scrubbing of HF via calcium oxide beds can be an efficient removal technique. A calcium utilization efficiency approaching unity can be attained. The interrelationship of the variables that result in the high efficiency is not completely understood. Temperature, humidity, and HF concentration all affect

Table 3. Particle size distribution of reacted bed from test No. 12. Data are for the center basket.

Fraction	Sieve size (mesh)	Particle size (μm)	Weight (g)	Wt % of stated size	Wt % less than stated size
1	+10	+2000	14.3	27.34	---
2	-10+20	-2000+850	10.9	20.84	72.66
3	-20+30	-850+600	4.8	9.18	51.82
4	-30+40	-600+425	4.6	8.80	42.64
5	-40+45	-425+355	3.0	5.74	33.84
6	-45+70	-355+212	4.4	8.41	28.10
7	-70+80	-212+180	1.9	3.63	19.69
8	-80+100	-180+150	3.0	5.74	16.06
9	-100	-150	5.4	10.33	10.32
			Net = 52.3 g		

Table 4. Summary of HF removal results via reaction with pebble quicklime.

Test	Calcium conversion[a] (%)	HF loading at test end (gHF/gBed)	Mass balance closure (%)	
			Ca	HF
5	46	--	NA[b]	NA
6	47	0.30	NA	-6.0
7	37	0.26	+1.8	+5.7
8	72	0.50	+4.2	NA
9	70-80	0.48-0.56	-0.3	NA
10	54	0.37	+0.4	NA
11	43	0.30	+6.0	+10
12	90	0.63	-7.0	+11

[a]Percent available calcium converted to CaF_2.

[b]NA = data not available.

the final bed utilization efficiency. Further studies to elucidate the relationship between mass transfer and chemical reaction would be worthwhile.

The mechanical properties of the bed appear such that the aspect ratio (L/D) must be maintained below approximately eight in the 1-in. diam system to avoid plugging problems. How this effect scales to larger systems is unknown. If a system is to be constructed in the plant, it is recommended that one full-scale reactor be tested under laboratory conditions such that solids handling characteristics will be better understood.

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