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ENGINEERING AND COST EFFECTIVENESS STUDY OF FLUORIDE EMISSIONS CONTROL

(FINAL REPORT)

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3.12 HF PRODUCTION

3.12.1 General

Manufacturing processes for fluorine, hydrogen fluoride, and derivative chemicals differ in two important respects from all other processes discussed in this report. First, the fluorine involved is a portion of both raw material and product. This creates an economic incentive to minimize fluoride losses. Second, the quantity and concentration of toxic fluorides constitutes a potential hazard which requires treatment to preclude adverse legal and regulatory action.

3.12.2 Industry Description

Figure 3-56 presents a flow schematic[4276,4242,4223,4261] and mass balance for the production of HF at the rate of 25 tons per day (50% anhydrous HF, 25% each of 50% and 80% HF).

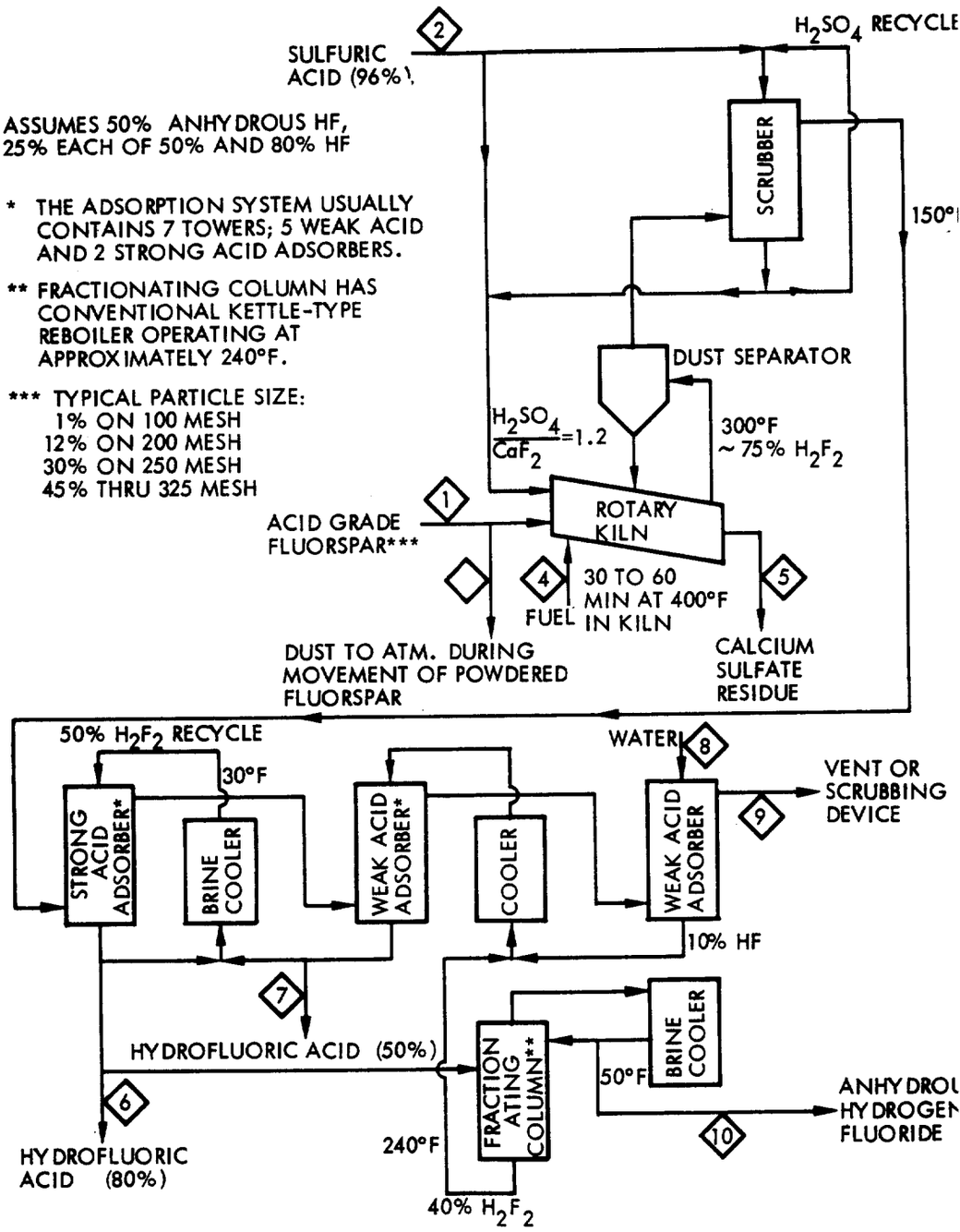
3.12.3 Production Trends

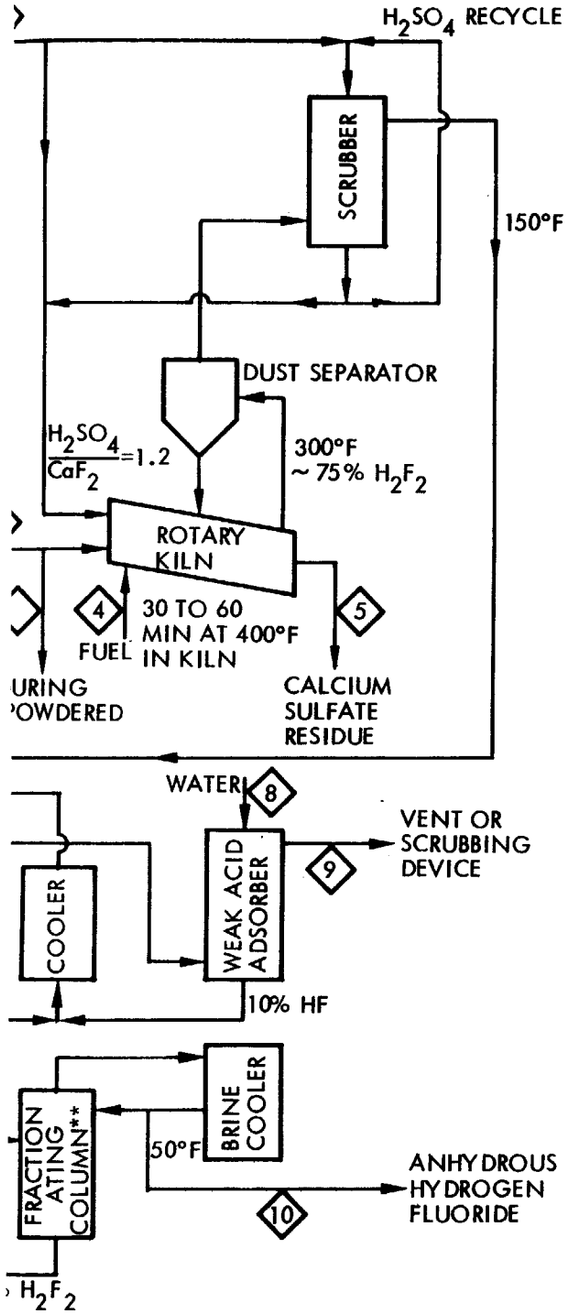
The historical growth of HF production has been 7.8% annually for the period 1959 to 1969.[4296] HF consumption for aluminum fluoride and synthetic cryolite production (used in manufacture of aluminum) plus the growing fluorocarbon market will tend to keep HF demand high. Expected growth rates between 5% and 7% are seen during the next few years.[4296] If these rates are extrapolated to the year 2000, HF production (as anhydrous HF) will increase from 337,000 tons in 1970 to between 1,430,000 and 2,565,000 tons.

3.12.4 Fluoride Emission Control Techniques

Hydrofluoric acid plant stack gas control systems are normally integral with the manufacturing process. Collection and transport systems are in-line extensions of the production system to the fluoride effluent control system. The spent charge from the kiln must be treated properly to prevent evolution of residual HF, but collection systems are not typically used for control of spent charge emissions.

Figure 3-57 presents a typical control installation using water scrubbing for a 25 ton per day plant. Either wet or caustic scrubbers are added as a final plant stage to act as a final HF removal step.


ASSUMES 50% ANHYDROUS HF, 25% EACH OF 50% AND 80% HF
* THE ADSORPTION SYSTEM USUALLY CONTAINS 7 TOWERS; 5 WEAK ACID AND 2 STRONG ACID ADSORBERS.
** FRACTIONATING COLUMN HAS CONVENTIONAL KETTLE-TYPE REBOILER OPERATING AT APPROXIMATELY 240°F.
*** TYPICAL PARTICLE SIZE:
1% ON 100 MESH
12% ON 200 MESH
30% ON 250 MESH
45% THRU 325 MESH
2
SULFURIC ACID (96%)
H_2SO_4 RECYCLE
SCRUBBER
150°F
DUST SEPARATOR
H_2SO_4/CaF_2=1.2
300°F
~ 75% H_2F_2
1
ACID GRADE FLUORSPAR***
ROTARY KILN
4
FUEL
30 TO 60 MIN AT 400°F IN KILN
5
DUST TO ATM. DURING MOVEMENT OF POWDERED FLUORSPAR
CALCIUM SULFATE RESIDUE
50% H_2F_2 RECYCLE
30°F
WATER
8
VENT OR SCRUBBING DEVICE
9
STRONG ACID ADSORBER*
BRINE COOLER
WEAK ACID ADSORBER*
COOLER
WEAK ACID ADSORBER
10% HF
7
HYDROFLUORIC ACID (50%)
FRACTIONATING COLUMN**
BRINE COOLER
50°F
ANHYDROUS HYDROGEN FLUORIDE
10
6
HYDROFLUORIC ACID (80%)
240°F
40% H_2F_2



BASIS - 25 TONS/DAY HF PRODUCTION (ASSUMES 50% ANHYDROUS HF, 25% EACH OF 50% AND 80% HF)

PROCESS STREAMS -LBS/HR

Material	Stream Numbers									
	1	2	3	4	5(B)	6	7	8	9*	10
HF SiF_4 CaF_2	4100(s)(C)		20(s)(D)		40(s)(C)	510 (1)	510 (1)		26 (g)(D) 34 (g)(D)	1010(C)
Total Fluorides Total as F	4100 2000		20 10		40 20	510 480	510 480		60 50	1010 960
$CaCO_3$ SiO_2 S H_2SO_4 (96%) $CaSO_4$ CO_2 SO_2 H_2O Fuel	40(A) 40(A) 2(A) 4(A) 	5400		7x10^{6}BTU	20 7100 	 130 	 510 	 400 	 16(g) 3(g) 	
Approx. Total Stream	4200	5400	20	--	7100	640	1000	400	80	1010

*Gaseous effluent stream

(A) Impurities in the fluorspar feed.

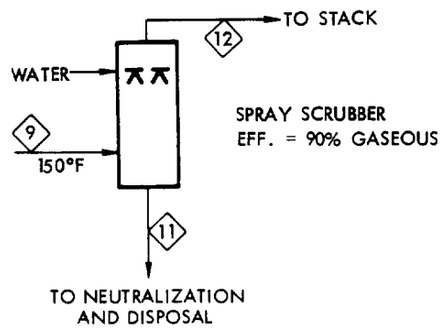
(B) The calcium sulfate residue stream may liberate fluorides. Literature search revealed no data.

(C) References 4242, 4259

(D) Reference 4261

Soluble fluoride evolution factor = 52 lb F/ton HF

Figure 3-56. Hydrofluoric Acid Production -



BASIS - 25 TONS/DAY HF PRODUCTION
(ASSUMES 1/2 ANHYDROUS HF, 1/4 50% HF AND 1/4 80% HF PRODUCED)

PROCESS STREAMS - LB/HR

Materials	Stream Number		
	9	11	12*
HF	26(g)	24(g)	2(g) (Est.)
SiF_4	34(g)	31(g)	3(g) (Est.)
Total Fluorides	60	55	5
Total as F	50	46	4
CO_2	16(g)		16(g)
H_2O	3(g)	2.5 (al)(A)	0.5(g)
Approx. Total Stream	80	60(A)	20

*Gaseous Effluent Stream

(A) Plus scrubbing water.

(B) Assumes 100% usage of scrubbers on all facilities.

Source	Soluble Fluoride Emission Factor - lb F/ton HF
Scrubber	4.1
Assumed Fugitive	0.0
Total Emission	4.1

Overall soluble fluoride emission = 4.1 lb F/ton HF(B)

Figure 3-57. HF Production - Controlled Process Model

3.12.5 Fluoride Emissions

Soluble fluoride emissions will increase from 700 tons (as F) in 1970 to about 5330 tons in 2000 at current abatement levels. If 99% control devices are employed, the fluoride emission will drop to 680 tons in the year 2000. These data are summarized in Table 3-104.

3.12.6 Economic Analysis

Table 3-105 presents the estimated economics of HF production at three plant capacities (5, 25, and 80 tons per day). Returns on investment for the three plants prior to the use of fluoride controls are 0.5%, 32.5% and 58.1%, respectively.

3.12.7 Impact of Control

Table 3-106 indicates the estimated costs of fluoride pollution control for a 25 ton per day plant. Impact on ROI is estimated as a ΔROI of about -0.5% for the 25 ton per day plant size.

Table 3-104. Soluble Fluoride Emissions from HF Production

	1970	2000
HF Production (10^6 tons/year)	0.34	2.60
Soluble Fluoride Evolution Factor (lb F/ton HF)	52	52
Soluble Fluoride Emission Factor with Current Practice (lb F/Ton HF)	4.1	4.1
Soluble Fluoride Emission Factor with 99% Control (lb F/ton HF)	--	0.52
Soluble Fluroide Evolution (10^3 tons F/year)	8.84	67.6
Soluble Fluoride Emission with Current Practice (10^3 ton F/year)	0.70	5.33
Soluble Fluoride Emission with 99% Control (10^3 ton F/year)	--	0.68

Table 3-105. Estimated Economics of Hydrofluoric Acid Production (excluding pollution control cost)

	Plant Capacity		
	5 Tons/Day	25 Tons/Day	80 Tons/Day
Capital Investment			
Installed Capital[A]	1.4 $MM	3.2 $MM	6.9 $MM
Off Sites	0.6	1.3	2.8
Total Capital Investment	2.0	4.5	9.7
Production Costs			
Direct Costs			
Fluorspar (acid grade: 2.02 tons/ton 100% H_2F_2 at 56.39)	113.91 $/ton H_2F_2	113.91 $/ton H_2F_2	113.91 $/ton H_2
Sulfuric Acid[B] (2.0 tons 100%/ton 100% H_2F_2 at $12.86 $/ton)	25.72	25.72	25.72
Fuel (6720 std. cu ft/ton 100% H_2F_2 at $0.35/1000 std. ft^3)	2.35	2.35	2.35
Water (2200 gal/ton 100% H_2F_2 at $0.40/$10^3$ gal)	0.88	0.88	0.88
Electric Power (450 kwh/ton 100% H_2F_2 at 0.007 $/kwh)	3.15	3.15	3.15
Operating Labor (4 men/shift)	76.80	15.36	4.80
Supervision and Fringe Benefits	38.40	7.68	2.40
Maintenance and Supplies	18.32	7.93	4.58
Total Direct Cost	279.53	176.38	157.07
Indirect Costs			
Depreciation (at 10%)	121.21	54.55	36.74
Interest (at 7%, 20% Debt)	16.97	7.64	5.14
Local Taxes and Insurance	30.30	13.64	9.19
Plant and Labor Overhead	92.16	18.43	5.76
Total Indirect Costs	260.64	94.26	56.83
Total Manufacturing Cost ($/ton 100% H_2F_2)	540.17	270.64	213.89
General and Sales Expenses ($/Ton 100% H_2F_2)	10.80	5.41	4.28
FOB Cost ($/Ton 100% H_2F_2)	550.97	276.05	218.17
Product Revenue ($/ton 100% H_2F_2)	560.00	560.00	560.00
Profit After Taxes (at 50%)	4.52 $/ton H_2F_2	141.98 $/ton H_2F_2	170.92 $/ton H_2F_2
Cash Flow ($MM/yr)	0.21 $MM/yr	1.6 $MM/yr	5.5 $MM/yr
Return on Investment[C]	0.5%	32.5%	58.1%

(A) Capital for sulfuric acid plant not included.
(B) Sulfuric acid plant collocated.
(C) Assumes 80% equity funding.

Table 3-106. Hydrofluoric Acid Production-Estimated Economics of Control Process

Basis - 25 tons per day of HF (assumes 50% anhydrous HF and 25% each of 50% and 80% HF produced.

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SPRAY SCRUBBER, 1 ft - 6 in. diameter by 8 ft, monel clad, 50 ft^3/min, 8 ft/sec max velocity, 2 gal/min, 2 in W.G.	5	4383 4391 4392	1.77		8
					Capital Subtotal	8
					Indirects (@ 15%)	1
					Contingency (@ 20%)	2
					Total Capital (as of January 1971)	11

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.01	0.25		0.26
Subtotal				0.26
Water(21)	(2 gpm, 0 recycle		)	0.01
Disposal(22)				----
Total Operating Cost				0.27

Total Operating Cost ($/hr)	0.27
Taxes and Insurance (2%, 330 days)	0.03
Capital (9.1%, 330 working days)	0.13
Pollution Control Cost ($/hr)	0.43
Pollution Control Cost(a) ($/ton)	0.41

(a) $/ton HF

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.