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HYDROFLUORIC ACID SCRUBBER SYSTEMS

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
INTRODUCTION	1
SUMMARY	1
EXPERIMENTAL	2
EQUIPMENT	2
REAGENTS	2
RESULTS AND DISCUSSION	4
ABSORPTION OF HYDROFLUORIC ACID	4
SOLIDS FORMATION WITH HYDROFLUORIC ACID	5
ACKNOWLEDGMENTS	7
REFERENCES	7

ABSTRACT

Caustic or aluminum scrubber solutions remove hydrogen fluoride from off-gas streams. Solids which appear with aluminum could be avoided by heating the scrubber solution.

HYDROFLUORIC ACID SCRUBBER SYSTEMS

INTRODUCTION

Each year over a million gallons of water are used to scrub hydrogen fluoride (HF) vapors from waste off-gas streams.^[1,2] Use of other potential scrubber solutions such as potassium hydroxide (KOH), aluminum nitrate nonahydrate (ANN), and monobasic aluminum nitrate (monoban) would result in significant volume reductions. A laboratory study was initiated to (1) demonstrate the effectiveness of these scrubber solutions to sorb HF, (2) determine if unexpected reactions occurred at flowsheet conditions, and (3) determine the consequences of deviation from flowsheet conditions.

SUMMARY

Caustic or aluminum scrubber solutions removed greater than 99% HF from simulated off-gas streams. Two potential problem areas were observed:

- Rapid HF addition rates could increase the temperature of KOH to near boiling.
- Solids appeared in aluminum scrubber solutions when the fluoride:aluminum molar ratio exceeded 1.6.

When the aluminum scrubber solutions were heated, a fluoride:aluminum molar ratio of 5.8 could be achieved with no solids formation.

EXPERIMENTAL

EQUIPMENT

An HF lecture bottle was warmed in a 50 °C water bath to vaporize liquid HF. Scrubber solutions were pumped at 30 liters/hour through a laboratory water aspirator jet which drew HF from the lecture bottle. The jet emptied into a 1-liter graduated cylinder from which scrubber solution was recycled through the pump and jet (see Figure 1). A slight vacuum was placed on the graduated cylinder to draw unreacted HF through a secondary scrubber containing caustic.

An AlF_3 precipitation study was performed by mixing different ratios of F and Al in 250-cc glass bottles. When solids were obtained, they were filtered through a Whatman 42 filter, dried, and weighed.

REAGENTS

Anhydrous hydrofluoric acid was obtained in a lecture bottle from Matheson Gas Products. The bottle contained 3 1/4 lb of 99.9% hydrofluoric acid. Scrubber solutions were prepared by using Baker and Adamson reagent grade potassium hydroxide pellets, Chevron Chemical Company 50% aluminum nonahydrate solution, or Chevron Chemical Company monobasic aluminum nitrate solution (monoban). The monoban was originally a 3.5 molar solution; however after standing for over a year, some crystallization had occurred--reducing the molarity to near 3. Studies of solid formation at different F:Al ratios used aliquots of 48% hydrogen fluoride (analytical reagent from Mallinckrodt Chemical Works) and the above aluminum solutions.

FIGURE 1
HYDROFLUORIC ACID SCRUBBER SYSTEM

RESULTS AND DISCUSSION

ABSORPTION OF HYDROFLUORIC ACID

Five runs were made with 5.45M KOH (see Table I).

TABLE I
ABSORPTION OF GASEOUS HF

Run	Time min	Scrubber Volume liters	Initial Moles	Final ^a Moles	HF Added ^b moles	Temperature °C	HF in 1M NaOH moles
Absorption with KOH							
1	30	1	5.45 (OH)	4.56 (OH)	0.88	-	0
2	10	1	4.56	0.88	3.63	90	0.03
3	20	0.97	0.75	0 ^c	1.2	-	0
4	20	0.5	2.75	0.09	2.5	60	0
5	15	0.4	0.09	0 ^d	0.93	35	0
Absorption with MONOBAN							
1	30	0.5	1.69 (Al)	-	1.75	45	0
Absorption with ANN							
1	30	1.0	1.75	-	1.7	36	0
2	60	1.0	1.75	-	2.3	40	0
3	60	1.0	1.75	-	2.4	40	0.04

^a Determined by titration.

^b Determined by HF cylinder weight loss.

^c pH = 6.

^d pH = 7.

The first three runs used the same one liter of KOH at three different HF addition rates (0.033, 0.36, and 0.06 moles HF per liter per min, respectively). Run 2 resulted in excessive turbulence and a 90 °C temperature within 10 minutes. The heat of reaction for HF and KOH was calculated to be -26.9 Kcal/mole.^[3,4] White HF fumes escaped from the primary KOH scrubber and were analyzed in the secondary NaOH scrubber. Runs 4 and 5 used 0.5 liter of fresh 5.45M KOH with HF addition rates of 0.25 and 0.15 moles per liter per min, respectively. The temperature of the KOH in Run 4 reached 60 °C in 20 min; the temperature

in Run 5 reached 35 °C in 15 min. Complete absorption of HF was demonstrated in all except Run 2.

A single run showed that 3M monoban scrubber solution completely absorbed 0.12 moles HF per liter per minute. The scrubber solution temperature reached 45 °C in 30 min. The final fluoride:aluminum ratio was 1 (see Table 1).

Three runs with one liter of 50% ANN (1.75M Al) yielded increasing F:Al molar ratios of 1, 2.3, and 3.6. In the first run complete HF absorption occurred with a final temperature of 36 °C. When the F:Al molar ratio reached 2.3, finely suspended solids were observed with no apparent loss in HF absorption. By the time the F:Al molar ratio reached 3.6, HF absorption was incomplete and a large amount of white, finely suspended solids slowed down recirculation rates. Upon settling out, the solids formed a 20 vol% jelly-like mass which after two days required forceful stirring to break up.

SOLIDS FORMATION WITH HYDROFLUORIC ACID

Fluoride-to-aluminum molar ratios exceeding 1.6 yielded solids at room temperature (Table II). However, when the HF was combined with ANN or monoban at 90 °C and then cooled to room temperature, solids did not appear until an F:Al molar ratio of 1.9 was exceeded. A solids-free solution with an F:Al ratio of 5.76 was obtained with a temperature of 90 °C. If the aluminum scrubber solution could be maintained at 90 °C, then almost six moles of fluoride per one mole of aluminum could be held in solution without solids formation. One of the previous scrubber runs indicated poor HF absorption with F:Al ratios of 3 to 4; however in that case the scrubber temperature was only 40 °C and some AlF_3 solids had formed.

TABLE II
SOLIDS FORMATION AT DIFFERENT FLUORIDE-TO-ALUMINUM RATIOS

Scrub Solution	Temp °C	F:Al Mole Ratio	Observations	% Theo. Solids
1.78M ANN	25	0.96	Clear.	0
1.78M ANN	25	1.28	Clear.	0
1.78M ANN	25	1.6	Clear.	0
1.78M ANN	25	1.76	Cloudy.	<5
1.78M ANN	25	1.92	Trace solids.	19
1.78M ANN	25	2.88	Solids.	82
1.78M ANN	25	3.84	Some solids.	52
1.78M ANN	25	4.8	Some solids.	44
1.78M ANN	25	5.76	Some solids.	38
1.78M ANN	25	1.9	Solids at 25 °C, clear when heated to 90 °C.	NM*
1.78M ANN	90	1.9	Clear, even after cooling to -10 °C.	NM
1.78M ANN	90	2.88	Clear, trace solids when cooled overnight.	NM
1.78M ANN	90	1.9	Gradual cool, no solids at 22 °C.	NM
1.78M ANN	90	1.9	Rapid cool to 22 °C, no solids.	NM
1.78M ANN	90	5.76	Clear, gradual cool, solids 50 to 70 °C.	NM
1.78M ANN	90	5.76	Clear, rapid cool, trace solids, more with standing.	NM
1.78M ANN	90	1.9	Rapid cool, 1 part added to 10 parts CAW, no solids, 22 °C.	NM
1.78M ANN	90	5.76	Rapid cool, 1 part added to 10 parts CAW, no solids, 22 °C.	NM
0.3M MONOBAN	22	0.6	Clear for weeks.	0
0.3M MONOBAN	22	1.1	Clear for weeks.	0
0.3M MONOBAN	22	1.7	Trace solids after 3 days.	0.6
0.3M MONOBAN	22	2.3	Trace solids; slowly increase.	39
0.3M MONOBAN	22	2.8	Solids, slowly increase.	54
0.3M MONOBAN	22	3.4	Solids, slowly increase.	100
0.3M MONOBAN	90	1.7	Gradual cool, no solids.	0
0.3M MONOBAN	90	1.7	Rapid cool, no solids.	0
0.3M MONOBAN	90	2.8	Gradual cool, trace solids in 4 hr.	10
0.3M MONOBAN	90	2.8	Rapid cool, trace solids in 4 hr.	10

* NM = not measured.

Disposal of the 90 °C solution was a potential problem because solids appeared when the temperature decreased to the 50 to 70° range. This problem was solved by blending one part of 90 °C scrubber solution (F:Al = 5.76) to 10 parts of a high-salt waste stream (0.5 to 1.0M Al). The combined solutions contained an excess of aluminum and yielded a solids-free waste solution at room temperature.

Such a high-aluminum waste stream was an ideal feed for fluidized bed calcination.

Monoban was commercially available in a higher concentration of aluminum (3.5M) than 50% ANN (1.75M Al). Thus the use of monoban would reduce the volume of scrubber solution for ultimate disposal.

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