

## Two-Step Ammoniation of By-Product Fluosilicic Acid to Produce High Quality Amorphous Silica

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**Abstract**—A two-step ammoniation was applied to neutralize the fluosilicic acid generated in the production of super-phosphate fertilizer, and to recover high-quality amorphous silica in the second step. A fluosilicic acid solution at 12.6% or 25.3 wt%  $\text{H}_2\text{SiF}_6$  was reacted with aqueous ammonia, precipitating silica and subsequently leaving  $\text{NH}_4\text{F}$  behind in the filtrate. Based on a fixed total of 7.2 moles of ammonia per mole of  $\text{H}_2\text{SiF}_6$  (120% stoichiometry), ammonia at a molar ratio of ammonia to  $\text{H}_2\text{SiF}_6$  of 2 to 6 was charged in the first step and the balance of 5.2-1.2 in the second step in four combination sets of ammonia addition. At a combination of 3 and 4.2 molar ratios in the respective first and second steps, amorphous silica of 99.7% purity was readily produced in the second step while a majority of the impurities were precipitated in the first step. The two-step ammoniation was near completion despite a non-equilibrium reaction. However, rapid ammoniation favored the crystallization of ammonium fluosilicate. A sharp pH change occurred between 1.5 and 2.5  $\text{NH}_3/\text{H}_2\text{SiF}_6$  molar ratios, indicating the rapid disappearance of  $\text{SiF}_6^{2-}$  ion from the solution.

Key words: Ammoniation, Amorphous Silica, Ammonium Fluosilicate, Fluosilicic Acid, Purity

### INTRODUCTION

Silica is a two-element compound containing oxygen and silicon as the most abundant elements on earth. The occurrence of silica separately or in combination with other oxides occupies approximately 60% of the earth's crust. Silica including quartz crystal has a variety of uses as a raw material for ceramics, construction, as well as silicon semiconductors. Also, silica in different types and shapes is popularly utilized for desiccants, absorbents, fillers, reinforcing agents, catalyst supports, piezoelectric crystals, integrated circuit (IC) sealants, optic fiber glass, and carriers and containers for semiconductors.

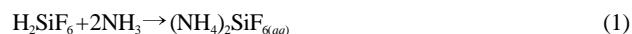
High-quality natural quartz is in short stable supply. Melt pulverization of natural quartz alone is impossible to reduce the content of radioactive elements such as uranium and thorium which could cause soft errors of IC [Tsugeno et al., 1991]. Also, current commercial processing of synthetic silica such as oxyhydrogen flame and the sol-gel technique is relatively costly. Therefore, the increased demand for low-cost, high-purity synthetic quartz in the electronic industry has resulted in the active exploration for alternative sources of silica.

Silicon tetrafluoride-containing gas, an undesirable polluting source, is liberated in the manufacture of phosphate fertilizers. In general plant practice, the liberated gas is absorbed in the process water to collect fluosilicic acid. In the past, most of this fluosilicic acid was neutralized with lime and discarded in storage ponds. More recently, a plant has supplied this acid to local water supply facilities as a fluorization chemical alternative to am-

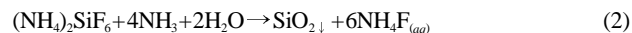
monium fluoride [Min, 1997]. Namhae Chemicals, the largest phosphate fertilizer plant in Korea, annually produces about 15,000 tons of such fluosilicic acid on a 100% basis.

The by-product fluosilicic acid generated in phosphate fertilizer plants is regarded as a major silicon-containing source [Blake and Stickney, 1966]. The ammoniation of fluosilicic acid to recover silica has been the subject of some investigators over the last 30 years [Tsugeno et al., 1991; Chieng, 1991; Aulich et al., 1984; Spijker, 1983; Nickerson and Burkert, 1966]. In particular, the particle size and its distribution, and the morphology of silica produced by ammoniation were extensively studied by Dragičević and Hraste [1993, 1994].

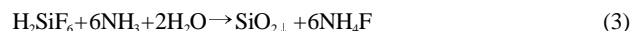
Theoretically, fluosilicic acid is first reacted with ammonia to form soluble ammonium fluosilicate:



The ammonium fluosilicate formed is reacted with additional ammonia to precipitate silica, leaving ammonium fluoride in the solution:



The overall neutralization of fluosilicic acid with ammonia can be written as follows:



In this investigative work, a two-step ammoniation was applied to neutralize fluosilicic acid and to recover high-grade amorphous silica in the second step. The determination of the molar ratio of ammonia to fluosilicic acid in each step was the major objective of this investigation for the purpose of gaining a satisfactory purity. This amorphous silica can be further purified during crystallization

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**Table 1. Chemical composition of Namhae fluosilicic acid (in ppm)**

Si	Ca	Fe	K	Al	Na	Mg
4.83%	564	156	133	94	80	22
Cr	Ni	Ba	Zn	Ti	Mn	V
19	7.3	7.2	2.8	2.5	2.1	1.7
Sr	Pb	Cu	Co	Cd	Li	-
1.1	1.0	0.21	0.15	0.1	0.05	-

to quartz under hydrothermal conditions [Private Conversation with Panasyuk, 1998]. Also, a scale-up investigation was made in an effort to develop a viable process, including the acquisition of necessary data for a commercial-scale ammoniation operation.

## EXPERIMENTAL

### 1. Raw Materials

A fluosilicic acid solution was collected from Namhae Chemical's fertilizer plant in the Yoechun Industrial Complex. The chemical composition of the feedstock was analyzed with an inductively coupled plasma (ICP), shown in Table 1.

The chemical analysis revealed that the feedstock contained an appreciable amount of major impurities such as Ca, Fe, K, Al and Na. Its concentration of  $\text{H}_2\text{SiF}_6$  was determined to be 25.3 wt% (2.2 mol/dm<sup>3</sup>) by the free acid method involving repeated titrations with a standard NaOH solution, first at a cold temperature with the addition of saturated  $\text{KNO}_3$  and then upon boiling.

### 2. Apparatus and Experimental Procedure

A teflon beaker and polypropylene tubes were used due to the corrosive nature of fluosilicic acid. Two concentration levels of the fluosilicic acid were used: 25.3 wt% and 12.6 wt%. The fluosilicic acid "as received" in the amount of 152 ml was used in all the beaker tests. Based on a fixed total of  $\text{NH}_3$  to  $\text{H}_2\text{SiF}_6$  molar ratio (AFMR) of 7.2 (120% stoich.), ammonium hydroxide at 2-6 AFMR was charged into vigorously agitated feed in the first step and the balance at 5.2-1.2 AFMR in the second step. The total ammonia requirement had already been determined as 120% stoichiometry in preliminary tests. A predetermined amount of ammonium hydroxide solution was metered at 2 ml/min with a Masterflex pump. This flowrate was equivalent to approximately 1-2 parts of ammonia per 100 parts of the acid, depending on the acid concentration used. The temperature and pH of the solution were monitored. A schematic diagram for the neutralization

is shown in Fig. 1. Upon completion of the first step, the slurry obtained was filtered and the filtrate was recovered for the subsequent second step. The cake was washed with warm distilled water 5 times and then dried at 105 °C. The same procedure for the 1st-step ammoniation was applied for the second step. The dried precipitate was analyzed for phases by x-ray diffraction (XRD) and for impurities by the ICP technique. The degree of hydration of the amorphous silica formed was determined by calcining at 1,000 °C for 2 hr in a muffle furnace. Thermal gravimetric (TG) and differential thermal (DT) analysis up to 1,200 °C were also performed on a typical second-step silica. The mean particle size of the amorphous silica by volume was measured by the use of laser with a Malvern Master Sizer.

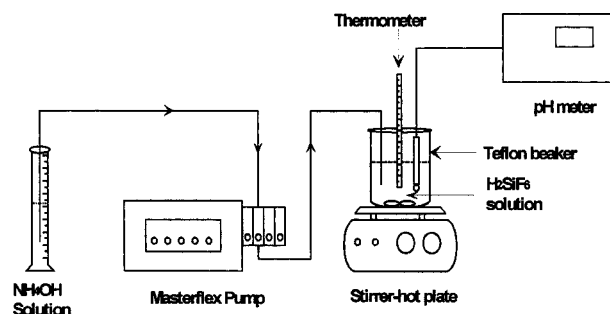
## RESULTS AND DISCUSSION

### 1. $(\text{NH}_4)_2\text{SiF}_6$ Crystallization in Rapid Ammoniation

In preliminary rapid ammoniation of a fluosilicic acid solution in the initial stage, it was found that the crystallization of  $(\text{NH}_4)_2\text{SiF}_6$  was dominant while the precipitation of silica was scarce. Therefore, to measure the amount of  $(\text{NH}_4)_2\text{SiF}_6$  crystallized, a 25% ammonia solution at an ammonia to  $\text{H}_2\text{SiF}_6$  molar ratio of 2-4 was added rapidly within several seconds into a fluosilicic acid feed at room temperature. The slurry formed was filtered, washed with acetone, dried and weighed. Acetone was used since the  $(\text{NH}_4)_2\text{SiF}_6$  crystal was insoluble in it. The dried solid was then treated in plenty of water for 2 hr to dissolve  $(\text{NH}_4)_2\text{SiF}_6$ . The remaining solid, being amorphous silica, was dried and weighed. The difference in weight between the first and second measurements should be the weight of the  $(\text{NH}_4)_2\text{SiF}_6$ . The conditions and results of the rapid ammoniation are shown in Table 2.

The  $(\text{NH}_4)_2\text{SiF}_6$  crystal formed in all three conditions consisted of 86-92% of the total solid. Evidently, the  $(\text{NH}_4)_2\text{SiF}_6$  in solution was crystallized as its solubility exceeded the limit at the temperature. Thus, the rapid ammoniation obviously favored reaction 1, causing a low silica yield. The declining  $(\text{NH}_4)_2\text{SiF}_6$  formation as AFMR increased was attributed to the fact that reaction 2 became more active at higher pHs. Based on this finding that ammonia flowrate or residence time was an important variable for thermodynamically complete ammoniation, the ammonia flowrate had to be as slow as possible. According to our study for the determination of optimum flowrate, a flowrate of 2 ml/min 25%  $\text{NH}_3$  was acceptable for eliminating  $(\text{NH}_4)_2\text{SiF}_6$  formation in the early stage.

### 2. Effect of Ammoniation Temperature on Filtration

**Fig. 1. A schematic diagram for ammoniation reaction.****Table 2. Rapid ammoniation of fluosilicic acid**

$\text{NH}_3/\text{H}_2\text{SiF}_6$ mol. ratio	2.0	3.0	4.0
$\text{H}_2\text{SiF}_6$ used, ml	76	76	76
25% $\text{NH}_4\text{OH}$ used, ml	25.2	37.7	50.3
Final pH	0.9	7.0	7.5
Filtrate volume, ml	65	45	43
Total solid wt, g	14.69	23.02	21.86
Amorph. silica wt, g	1.20	2.41	3.09
$(\text{NH}_4)_2\text{SiF}_6$ wt, g	13.49	20.61	18.77
% of total solid	92	90	86

**Table 3. Effects of temperature and concentration of  $\text{H}_2\text{SiF}_6$  solution on filtration of ammoniation product at a fixed  $\text{NH}_3/\text{H}_2\text{SiF}_6$  molar ratio of 3**

$\text{H}_2\text{SiF}_6$ conc., %	Initial $\rightarrow$ final temp., $^{\circ}\text{C}$	Final pH	Relative filtration rate	Solid wt., g	Solid phases
25.3	10 $\rightarrow$ 17	7.1	very slow	10.1	$(\text{NH}_4)_2\text{SiF}_6$ +minor amorph. silica
	26 $\rightarrow$ 47	7.0	medium	3.4	amorph. silica+trace $(\text{NH}_4)_2\text{SiF}_6$
	57 $\rightarrow$ 64	6.9	fast	3.6	amorph. silica
12.6	26 $\rightarrow$ 43	6.9	slow	3.7	amorph. silica+minor $(\text{NH}_4)_2\text{SiF}_6$

Ammoniation temperature was evaluated, based on how the  $(\text{NH}_4)_2\text{SiF}_6$  crystal formed in the early stage of ammoniation affected subsequent filtration. At a fixed AFMR of 3, a 38-ml  $\text{NH}_3$  solution was added at a 2 ml/min flowrate to a 76-ml  $\text{H}_2\text{SiF}_6$  feed-stock at different initial temperatures. An ice-water bath was employed for the study at a temperature lower than room temperature. The slurry formed in each ammoniation test was filtered under vacuum with a No. 41 Whatman paper and a Buchner funnel. The cake was washed with acetone, dried, weighed, and X-rayed. The results are shown in Table 3:

Most of the solids formed in the range 10-17  $^{\circ}\text{C}$  were  $(\text{NH}_4)_2\text{SiF}_6$  crystals similar to the results of rapid ammoniation, making its filtration very slow. The use of a diluted feed of 12.5%  $\text{H}_2\text{SiF}_6$  at room temperature was found to cause a slow filtration to some extent. Very fine silica particles were noticed in this case. The formation of  $(\text{NH}_4)_2\text{SiF}_6$  as well as fine silica was believably attributed to the slowness.  $(\text{NH}_4)_2\text{SiF}_6$  was crystallized at a minimum in the range 26-47  $^{\circ}\text{C}$  with a 25.3%  $\text{H}_2\text{SiF}_6$  solution, but not crystallized at all above 57  $^{\circ}\text{C}$ . In the light of the solubilities of natural  $(\text{NH}_4)_2\text{SiF}_6$  crystal being 18.6 and 55.5 g per 100  $\text{cm}^3$  of respective cold and boiling water [Weast and Astle, 1981-1982], the reaction temperature is considered as another key variable for successful ammoniation particularly at an early stage.

### 3. Two-Step Ammoniation at Different $\text{NH}_3/\text{H}_2\text{SiF}_6$ Molar Ratios (AFMRs)

On the base of a fixed total of 7.2 AFMR (120% stoich), ammonia addition was varied in the AFMR range of 2-6 in the first step and the balance of 5.2-1.2 in the second step. Four sets of the combination of AFMRs were selected: 2+5.2, 3+4.2, 4+3.2 and 6+1.2. The temperature and pH of the reacting solution were monitored. In case of 25.3%  $\text{H}_2\text{SiF}_6$ , all the 1st-step filtrates were warmed to 32-34  $^{\circ}\text{C}$  prior to the second step to prevent some  $(\text{NH}_4)_2\text{SiF}_6$  crystallization at room temperature. The results of the ammoniation tests with 25.3% and 12.6%  $\text{H}_2\text{SiF}_6$  solutions are listed in Tables 4 and 5, respectively.

The solid precipitated in all the tests was determined to be amorphous silica by XRD, showing a single broad peak. The total amount of silica formed at each AFMR combination ranged from 22.14 to 23.7 g. Considering that the water content of silica, including adsorbed (free) water, ranged from 5.5 to 14.2 wt% and the 20 g of anhydrous silica was to be formed theoretically, the silica yield was near completion in all the 4 sets. The yield was unaffected in the acid concentration range applied. Scholten and Montfoort [1983], however, reported a 30-40% reduction in the silica yield when a high-concentrated feed such as 30 wt%  $\text{H}_2\text{SiF}_6$  was employed.

The ammoniation resulted in increasing temperatures up to 48  $^{\circ}\text{C}$  due to the exothermic nature of the reaction. It was interesting to note that with a 12.6%  $\text{H}_2\text{SiF}_6$  solution, the portion of the silica formed at an AFMR of 2 in the first step was less than 1%,

**Table 4. Two-step ammoniation using a 25.3%  $\text{H}_2\text{SiF}_6$  solution**

$\text{NH}_3/\text{H}_2\text{SiF}_6$ molar ratio		2.0	3.0	4.0	6.0
First step	Initial $\rightarrow$ final temp., $^{\circ}\text{C}$	24 $\rightarrow$ 37	25 $\rightarrow$ 46	25 $\rightarrow$ 47	25 $\rightarrow$ 48
	Final pH	1.3	6.7	7.7	8.1
	Silica formed, g	2.04	7.67	12.4	19.89
	Spec. surf. area, $\text{m}^2/\text{g}$	27	66	70	34
	Mean particle size, $\mu\text{m}$	17	27	16	31
	Water content, %	5.5	7.6	8.2	9.4
	x value in $\text{SiO}_2 \cdot x\text{H}_2\text{O}$	0.19	0.27	0.30	0.35
	Wt. distribution ratio, %	9	33	52	84
$\text{NH}_3/\text{H}_2\text{SiF}_6$ molar ratio		5.2	4.2	3.2	1.2
Second step	Initial $\rightarrow$ final temp., $^{\circ}\text{C}$	33 $\rightarrow$ 38	32 $\rightarrow$ 37	32 $\rightarrow$ 34	34 $\rightarrow$ 35
	Final pH	8.4	9.0	9.1	9.3
	Silica formed, g	20.23	16.03	11.28	3.81
	Spec. surf. area, $\text{m}^2/\text{g}$	158.9	54.8	37.2	122.6
	Mean particle size, $\mu\text{m}$	123	42	40	31
	Water content, %	5.8	7.6	10.0	12.5
	x value in $\text{SiO}_2 \cdot x\text{H}_2\text{O}$	0.21	0.27	0.37	0.48
	Wt. distribution ratio, %	91	67	48	16
Total silica formed, g		22.27	23.70	23.68	23.70

**Table 5. Two-step ammoniation using a 12.6%  $\text{H}_2\text{SiF}_6$  solution**

First step	$\text{NH}_3/\text{H}_2\text{SiF}_6$ molar ratio	2.0	3.0	4.0	6.0
	Initial $\rightarrow$ final temp., $^{\circ}\text{C}$	24 $\rightarrow$ 37	24 $\rightarrow$ 40	23 $\rightarrow$ 39	23 $\rightarrow$ 39
	Final pH	1.2	6.5	8.1	8.4
	Silica formed, g	0.18	6.85	10.21	18.57
	Wt. distribution ratio, %	8	31	46	80
Second step	$\text{NH}_3/\text{H}_2\text{SiF}_6$ molar ratio	5.2	4.2	3.2	1.2
	Initial $\rightarrow$ final temp., $^{\circ}\text{C}$	24 $\rightarrow$ 34	23 $\rightarrow$ 30	24 $\rightarrow$ 28	24 $\rightarrow$ 26
	Final pH	8.8	8.8	9.0	9.3
	Silica formed, g	21.96	15.31	12.23	4.65
	Mean particle size, $\mu\text{m}$	5.2	6.0	10.5	14.2
	Wt. distribution ratio, %	99.2	69	54	20
Total silica formed, g		22.14	22.16	22.44	23.22

compared to 9% with 25.3%  $\text{H}_2\text{SiF}_6$  although the final pH was almost identical at pH 1.2–1.3. It was because  $(\text{NH}_4)_2\text{SiF}_6$  remained more stable in the lower concentrated solution, so reaction 1 was more favorable than reaction 2 at this pH.

The specific surface area and mean particle size of dried amorphous silica varied from 27 to 159  $\text{m}^2/\text{g}$  and from 15 to 123  $\mu\text{m}$ , respectively. The specific area and particle size of silica could hardly be related to the molar ratio due to inconsistent data. The values of silica specific area were quite small compared to that of commercially produced silica gel. Dragičević and Hraste [1994] reported that the value was no higher than 190  $\text{m}^2/\text{g}$  in the ammoniation of fluosilicic acid. They, however, concluded that a higher pH of ammoniation and more concentrated fluosilicic acid feed resulted in a lower specific area of silica.

Dried amorphous silica, known as xerogel, might not reflect the true size and morphology of silica in aqueous solution, called hy-

drogel, containing generally 70–80% free water because a hydrogel silica was reported to transform into a xerogel having a lower specific surface area [Dragičević and Hraste, 1994] due to the shrinkage of gel structure [Iler, 1979] during drying. Dragičević and Hraste [1993] also indicated that raising the  $\text{H}_2\text{SiF}_6$  concentration, residence time, pH and temperature caused the formation of larger silica particles.

#### 4. The Impurity Content of Silica in Two-step Ammoniation

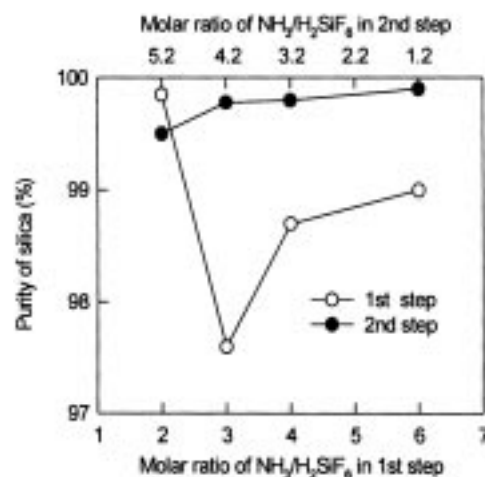
The impurity content of silica formed at different AFMRs is listed in Table 6. In case of 25.3%  $\text{H}_2\text{SiF}_6$ , a majority of Ca, Al and Mg was precipitated in the first step at 3 AFMR or above. For example, at 3 AFMR, 13,580 ppm CaO, 4,910 ppm  $\text{Al}_2\text{O}_3$ , and 1,310 ppm MgO in the first step were drastically lowered to 98 ppm CaO, 240 ppm  $\text{Al}_2\text{O}_3$ , and 27 ppm MgO in the second step. The Fe content was insufficiently lowered from 3,150 ppm to 1,570 ppm. It was interesting to note that an AFMR of 2 in the first step also yielded comparably low impurities; however, it was impractical to apply this AFMR due to such a low silica yield of 8%. The soluble impurities such as  $\text{K}^+$  and  $\text{Na}^+$  seemed unaffected by the two-step ammoniation.

The purity of silica formed in the two-step ammoniation of a 25.3%  $\text{H}_2\text{SiF}_6$  solution was estimated by simply taking the ma-

**Table 6. The Impurity content of silica in two-step ammoniation (in ppm)**

Conditions	CaO	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$
1. 12.6% $\text{H}_2\text{SiF}_6$ solution						
1st step: 2.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	n/a	n/a	n/a	n/a	n/a	n/a
2nd step: 5.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	4760	1060	2430	460	<12	89
1st step: 3.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	15400	3400	4570	1350	<12	65
2nd step: 4.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	80	710	1170	12.8	<12	73
1st step: 4.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	10900	2080	3720	500	<12	65
2nd step: 3.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	70	330	970	11	<12	47
1st step: 6.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	5880	1030	2720	490	<12	73
2nd step: 1.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	180	2640	160	30	<12	63
2. 25.3% $\text{H}_2\text{SiF}_6$ solution						
1st step: 2.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	500	416	300	78	33	54
2nd step: 5.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	490	1280	2430	480	23	85
1st step: 3.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	13580	4910	3150	1310	76	109
2nd step: 4.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	98	240	1570	32	28	76
1st step: 4.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	8120	1400	3140	730	<12	92
2nd step: 3.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	77	790	940	27	28	57
1st step: 6.0 $\text{NH}_3/\text{H}_2\text{SiF}_6$	5040	1740	2430	510	<12	69
2nd step: 1.2 $\text{NH}_3/\text{H}_2\text{SiF}_6$	72	208	200	10	<12	19

n/a: not available for analysis due to an insufficient amount of silica formed.

**Fig. 2. The purity of silica formed at different  $\text{NH}_3/\text{H}_2\text{SiF}_6$  molar ratios (25.3%  $\text{H}_2\text{SiF}_6$  solution).**

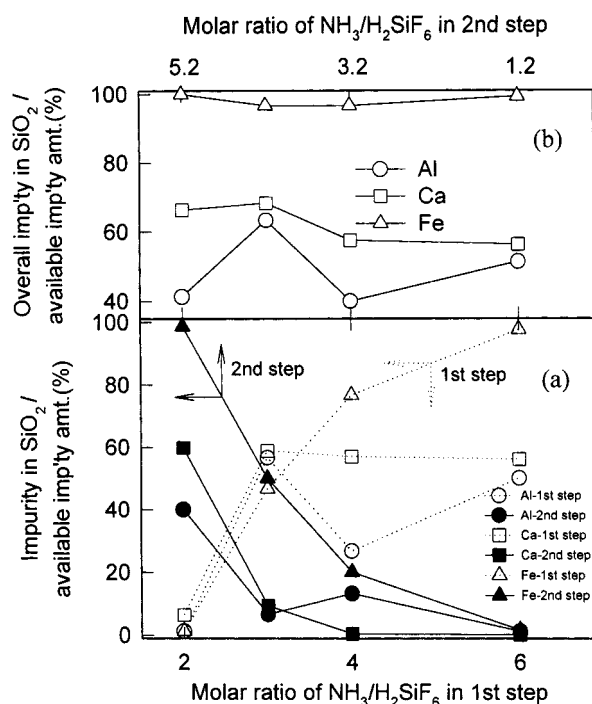


Fig. 3. The distribution ratio of major impurities at different  $\text{NH}_3/\text{H}_2\text{SiF}_6$  molar ratios (25.3%  $\text{H}_2\text{SiF}_6$  solution).

for impurities into account; this is shown in Fig. 2. A range of 99.5 to 99.9% purity could be obtained in all the AFMR combinations. In particular, at an AFMR combination of 3.0 and 4.2 in the respective first and second steps, a 99.78% purity silica was successfully obtained in the second step. This combination of molar ratio yielded second-step silica not only of high quality but of a reasonable yield distribution ratio of about 2/3 as indicated in Table 4. However, about 1/3rd of the silica had already been produced with only 97.5% purity in the first step. In conclusion, the two-step ammoniation was proven to be beneficial to seek a higher quality silica product at the expense of a lower silica yield.

### 5. Distribution Ratio of Major Impurities in Two-step Ammoniation

This study aimed to investigate how major impurities such as Al, Ca, Fe in the feed were redistributed during the course of the two-step ammoniation. Fig. 3(a) and 3(b) show the ratio of individual impurity of silica formed in each step and the overall impurity, respectively, to the amount initially available in the feed.

In case of Ca, about 60% of the available Ca was coprecipitated with silica above an AFMR of 2 in the first step. The overall Ca precipitation was in the range of 60-68%. The Fe precipitation increased almost proportionally with increasing AFMRs in the first step and decreased likewise in the second step. Therefore, almost all the Fe in the feed ended up in the silica at all the AFMR combinations. It can be concluded that the distribution of each impurity element in the ammoniation likely depends on its solubility product constant at the temperature [Weast and Astle, 1981-1982; Butler, 1964; Chemical Society, 1964].

### 6. Hydration of Amorphous Silica

The TGA curve of a typical amorphous silica formed in the second step is shown in Fig. 4. The weight loss in the TGA curve

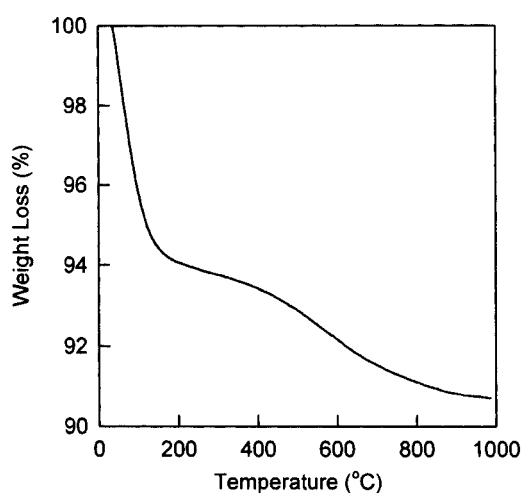


Fig. 4. The TGA curve of a typical amorphous silica formed in 2-step ammoniation.

was rapid up to about 150°C and then slowed down. The sharp weight loss was attributed to free water and the gradual loss indicated structured bound water. About 5.5% wt loss attributable to free water corresponded to a  $\text{H}_2\text{O}$  to  $\text{SiO}_2$  molar ratio (WSMR) of 0.2 and about 4.5% wt loss representing bound water to a WSMR of 0.16.

According to Iler's interpretation [1979] of the bound water vs. temperature curve originally presented by Thiessen and Koener [1930], the portion of the curve below 70°C involved adsorbed water and the portion above it represented the dehydration of the silanol group. Thiessen and Koener reported that the removal of adsorbed water required definite steps corresponding to 2.5, 2.0, 1.0, 0.5 molar ratios of water to silica. The removal of one layer of adsorbed water was, therefore, assumed to correspond to about 0.5 mol water per silica [Iler, 1979].

### 7. Morphology of Amorphous Silica Formed

Figs. 5(a) and 5(b) show scanning electron micrographs ( $\times 1000$ ) of amorphous silica formed at an AFMR combination of 3.0 and 4.2, respectively. Amorphous silica precipitated from the aqueous solution by condensation-polymerization existed as clusters or aggregates consisting of many smaller particles [Yoon and Ju, 1998]. Although the size of the initial individual particle was in the sub-micron range, particles formed open, three-dimensional gel networks to make a cluster known as a primary particle [Kirk and Othmer, 1982; Iler, 1979]. The first-step silica in Fig. 5(a) included some underdeveloped or incomplete clusters, whereas the second-step silica in Fig. 5(b) consisted of all well-developed and complete ones. The clusters formed in the first step were found to be finer and denser and thus less friable than the second-step silica.

### 8. Scale-up Tests in Two-step Ammoniation

Scale-up tests in two-step ammoniation were conducted only at a fixed combination of 3 and 4.2 AFMR in the respective first and second steps. Two levels of fluosilicic acid concentration, 12.6% and 25.3%  $\text{H}_2\text{SiF}_6$ , were applied. A 1500-ml feed or 3000-ml diluted one was mechanically agitated at 800 rpm in an acrylic reactor. In the first step, a 744-ml 25%  $\text{NH}_4\text{OH}$  solution was pumped into the solution at 20 ml/min for 38 min. The pH of the reacting

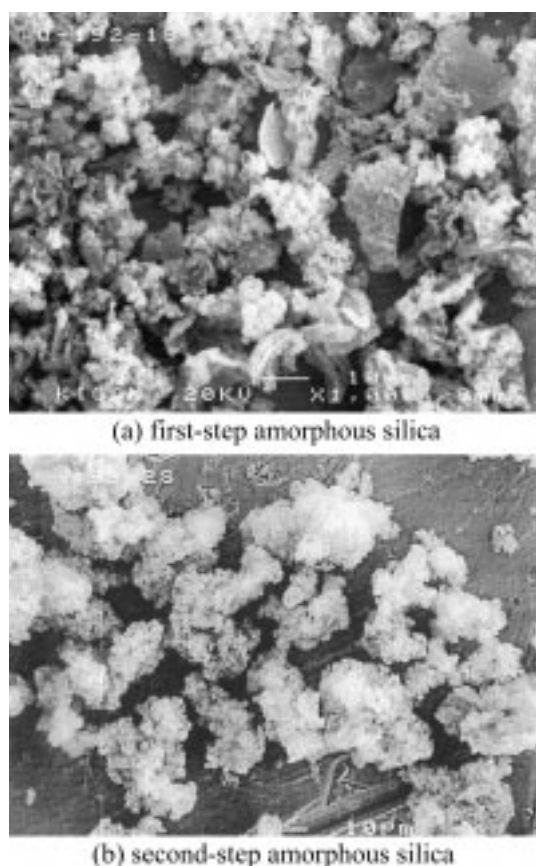


Fig. 5. SEM micrographs of amorphous silica in different ammoniation steps.

solution was monitored. Upon completion of the ammoniation, the slurry formed was vacuum-filtered and the cake was washed with about 600-ml warm demineralized water 5 times and dried at 105 °C. The filtrate was saved for subsequent second-step ammoniation. In the second step, a 1,042-ml ammonia solution was charged into the filtrate for 52 min. The rest of the procedure was the same

Table 7. Scale-up tests at an AFMR combination of 3.0 (1st step) and 4.2 (2nd step)

	H <sub>2</sub> SiF <sub>6</sub> concentration	25.3% H <sub>2</sub> SiF <sub>6</sub>	12.6% H <sub>2</sub> SiF <sub>6</sub>
First step	Initial → final temp., °C	27 → 65	28 → 54
	Final pH	6.1	6.0
	Filtrate volume, ml	1840	2900
	Silica formed, g	78	85
	Water content, %	6.9	7.6
	x in SiO <sub>2</sub> · xH <sub>2</sub> O	0.25	0.28
Second step	Initial → final temp., °C	33 → 47	31 → 44
	Final pH	9.0	9.0
	Filtrate volume, ml	2140	3040
	Silica formed, g	137	129
	water content, %	9.4	7.8
	x in SiO <sub>2</sub> · xH <sub>2</sub> O	0.35	0.28
Total silica formed, g		215	214
Silica yield, %		98	98

as mentioned earlier. The results of the scale-up tests are summarized in Table 7.

It was intended to compare the results of the scale-up tests with those of the beaker tests given in Table 4. A silica yield of 98% confirmed nearly complete ammoniation and the independence on the feed concentration. The temperature increase of the reacting solution in the first step was rapid with increasing AFMRs up to about 2 and then slowing down thereafter. Finally, the temperature reached a maximum of 65 °C with 25.3% H<sub>2</sub>SiF<sub>6</sub>, being 17 degrees higher than the beaker tests. An appreciable amount of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> crystallization in the first-step filtrate was also observed when it was cooled to room temperature, but the nearly complete silica yield reflected no relation to the crystallization. The chemical analysis of impurities in silica indicated that more Ca<sup>2+</sup> and less Al<sup>3+</sup> were precipitated in the first step, compared to those in the beaker tests. In conclusion, the purity of second-step silica was somewhat lowered in the scale-up tests: 99.78% vs. 99.7%. Also, the purity of silica from 12.6% and 25.3% H<sub>2</sub>SiF<sub>6</sub> feeds was comparable.

The filtration rate of the warm first-step silica slurry from a 25.3% H<sub>2</sub>SiF<sub>6</sub> solution was determined to be about 200 ml/min with a 15-cm ashless Whatman No. 41 paper and a 0.45 kw, 1-phase vacuum pump. However, a faster washing of the second-step silica at about 1,500 ml/min with warm distilled water was observed. The first-step silica slurry from a 12.6% H<sub>2</sub>SiF<sub>6</sub> solution took more time to filter than that from a 25.3% H<sub>2</sub>SiF<sub>6</sub> solution since it was not only finer, but contained some (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> crystal.

The pH change in relation to AFMR in the two steps is shown in Fig. 6. In the first step, a sharp pH rise up to 5.5 occurred between AFMRs of 1.5 and 2.5 and the pH change was retarded thereafter, reaching the final pH of 6.0–6.1 at an AFMR of 3. The rapid pH increase was attributed to the continuous formation of soluble (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> according to reaction 1. Then, the slow pH change afterward was affected by the prevailing formation of silica from (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> as indicated by reaction 2. Therefore, it was interesting to note that those two reactions were not clearly separated from each other at an AFMR of 2. Rather, reaction 1 prevailed at or below this ratio and reaction 2 became predominant above it. This finding was based on the fact that silica could be

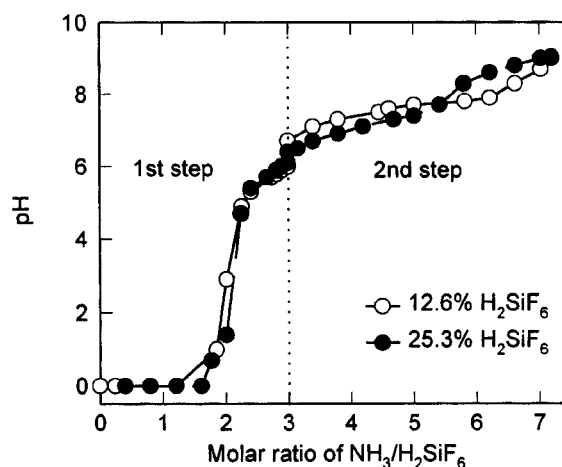


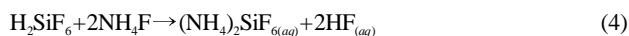
Fig. 6. Change of pH as a function of NH<sub>3</sub>/H<sub>2</sub>SiF<sub>6</sub> molar ratio in first and second steps.

formed even at pH 1 level when an AFMR of 2 was employed (refer to Tables 4 and 2). An investigation by Aulich et al. [1984] indicated that  $\text{SiF}_6^{2-}$  ion was stable up to a pH of about 3. The pH in the second step increased gradually, finally reaching pH 9 at an AFMR of 7.2.

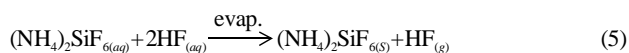
As shown in Fig. 6, the pH curves did not match at an AFMR of 3, because the pH values of the first-step slurry and its filtrate were different due to the effect of temperature. There was practically no difference in the pH dependence on AFMR between the two fluosilicic acid concentrations.

### 9. Preparation of Amorphous Silica by an $\text{NH}_4\text{F}$ - $\text{NH}_3$ Method

Amorphous silica could be prepared by an  $\text{NH}_4\text{F}$ - $\text{NH}_3$  method alternative to the two-step ammoniation practiced thus far. First, soluble  $(\text{NH}_4)_2\text{SiF}_6$  was formed by adding reagent-grade ammonium fluoride crystal at an  $\text{NH}_4\text{F}$  to  $\text{H}_2\text{SiF}_6$  molar ratio of 2.2 (110% stoich.) into a fluosilicic acid feed according to reaction 4:



The solution was then evaporated to dryness by heating it at about 200 °C on a hot plate, evolving HF gas and then  $(\text{NH}_4)_2\text{SiF}_6$  was crystallized by reaction 5:



The ammonium fluosilicate was washed with acetone and decanted 5 times, and redissolved in distilled water according to reaction 6:



Finally, amorphous silica was precipitated by charging ammonia at an AFMR of 4.8 (120% stoich.) into the ammonium fluosilicate solution as indicated earlier in reaction 2. The silica was subjected to chemical analysis for impurities.

According to the material balance of the overall reaction, the silica yield was determined to be 94%, which was lower than 98% by the 2-step ammoniation. This might be attributed to the incomplete crystallization of  $(\text{NH}_4)_2\text{SiF}_6$  by evaporation, leaving some  $(\text{NH}_4)_2\text{SiF}_6$  behind in the residual solution. Also, the silica had a 99.6% purity, containing more CaO and a little less  $\text{Fe}_2\text{O}_3$  impurities than the second-step silica formed previously.

To identify any impurities present in the  $(\text{NH}_4)_2\text{SiF}_6$  crystal obtained by reaction 5, its sample was characterized by XRD. Nothing but strong  $(\text{NH}_4)_2\text{SiF}_6$  peaks were identified, as shown in Fig. 7. Impurities below the detection level should, however, be trapped in the  $(\text{NH}_4)_2\text{SiF}_6$  lattice during the crystallization by evaporation.

Another sample of the  $(\text{NH}_4)_2\text{SiF}_6$  was heated up to 1,000 °C at a rate of 10 °C/min for TGA, and the results are shown in Fig. 8. First, a 5-7% weight loss occurred around 200 °C due to the dehydration of bound water. The  $(\text{NH}_4)_2\text{SiF}_6$  was then decomposed to  $\text{NH}_4\text{F}$ , evolving  $\text{SiF}_4$  gas between 220-310 °C. A total of about 55% weight was lost up to this temperature. Finally, the sublimation of  $\text{NH}_4\text{F}$  took place at about 850 °C. The thermal decomposition of  $(\text{NH}_4)_2\text{SiF}_6$  can be expressed by the following reactions:

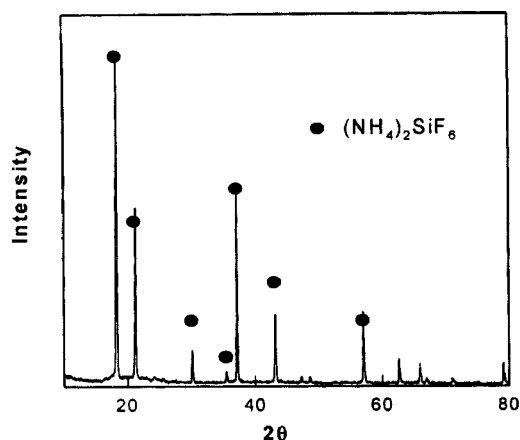


Fig. 7. X-ray spectra of  $(\text{NH}_4)_2\text{SiF}_6$  prepared.

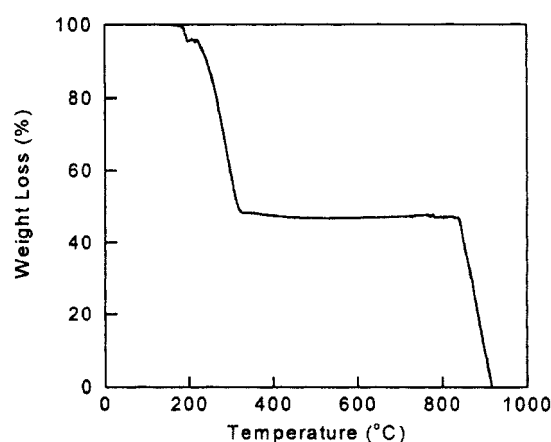


Fig. 8. TGA curve of  $(\text{NH}_4)_2\text{SiF}_6$  prepared.



## CONCLUSIONS

This investigation was made in an effort to develop a viable process including necessary data for a large-scale operation for the recovery of amorphous silica from fluosilicic acid by the two-step ammoniation. The conclusions can be summarized as the following:

1. An  $\text{NH}_3/\text{H}_2\text{SiF}_6$  molar ratio combination of 3 and 4.2 in the respective first and second steps is satisfactory to produce the second-step silica of 99.7% purity. The overall recovery of silica is near completion.

2. At this combination, a majority of the impurities such as Ca, Al, Mg are precipitated in the first step. The two-step ammoniation is less effective for the removal of Fe. About 70% Ca, 50% Al and almost all the Fe available in the feed are invariably co-precipitated with the overall silica, being likely to correspond to the individual solubility product constant at the temperature.

3. In the pH vs.  $\text{NH}_3/\text{H}_2\text{SiF}_6$  molar ratio curves, the solution pH

is raised sharply up to 5.5 between the 1.5 and 2.5 ratio and then slowed down thereafter, reaching a pH of 6 in the first step and pH 9 in the second step. The rapid increase in pH is attributed to the favorable formation of the soluble  $(\text{NH}_4)_2\text{SiF}_6$  and the slow pH change to the prevailing formation of silica from  $(\text{NH}_4)_2\text{SiF}_6$ .

4. It is noted that silica can be precipitated from the solution even at a pH of 1 where  $\text{SiF}_5^{2-}$  ion is stable.

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