International Fertilizer Industry Association

ISMA* Technical Conference

Orlando, Florida, USA
23-27 October 1978

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

Sodium Silicate and Calcium Fluoride from Sodium Fluosilicate

By

A.F. Sabry , Chairman
Societe Financiere et Industrielle D'Egypte
Kafr El Zayat - Egypt

Fluosilicic acid is the main by-product in all scrubbing processes involved in the phosphatic fertilizer industries . From the chemical point of view , it is an interesting complex acid which can undergo many reactions giving rise to several products. The acid itself , which contains about 80% fluorine, may be used in the fluorination of potable water . In the phosphatic fertilizer industry , it may be used in making fluorides such as sodium , aluminium or ammonium fluorides , or in the preparation of metal fluosilicates such as sodium or potassium fluosilicates. In our company , fluosilicic acid was utilized since 1940 in making sodium fluosilicate or silicofluoride, by reaction with sodium chloride solution .

$$H_2 Si F_6 + 2 Na Cl \longrightarrow Na_2 Si F_6 + 2 HCl$$

The precipitated sodium silicofluoride is washed , centrifuged , dried and crushed , wherely a product of 99% purity is obtained . The market of sodium fluosilicate was not stable enough to allow for a regular run of the unit , which was often stopped for long periods.

Sodium fluosilicate which is a complex acid salt of sodium fluoride and silicon fluoride 2Na F.Si F_4 , reacts with alkalies giving rise to fluorides and hydrated silica . The purpose of this investigation is to study the reactions which take place between sodium fluosilicate and lime , which is the cheapest alkali , and the possible products to be obtained . The reactions can be summarised as follows:-

$$1-Na_2 Si F_6 + 2 Ca (OH)_2 \longrightarrow 2 Ca F_2 + 2 Na F + H_2SiO_3 + H_2O$$

$$2-2NaF + Ca (OH)_2 \longrightarrow CaF_2 + 2NaOH$$

$$3-2Na OH + H_2 SiO_3 \longrightarrow Na_2 SiO_3 + 2H_2 O$$

The sum of the three reactions is :

$$Na_2SiF_6 + 3Ca(OH)_2 \longrightarrow 3CaF_2 + Na_2SiO_3 + 3H_2O$$

Commercially , calcium fluoride and sodium silicate are much more needed than sodium fluosilicate. A series of laboratory experiments was carried out to cover the study of the best conditions which leed to acceptable products. In each experiment , the weighed amount of sodium fluosilicate was added to the stated amount of water. Lime in the form of milk was added gradually with continuous stirring and continuous heating of the mixture.

Stirring was completed for 30 minutes at boiling temperature , followed by filteration . The precipitated calcium fluoride was well washed , and the filterate containging sodium silicate solution kept for analysis. It is clear that the main goals are :

1- To get the maximum percentage of calcium fluoride in the solid product.
2- To get the maximum concentration of sodium silicate in solution.

To arrive to the best conditions for achieving these goals , the main factors studied were :

a- Effect of CaO / Na_2SiF_6 ratio , where the ratio was changed just near the theoretical ratio .

b- Effect of dilution of reaction medium.

The results of the series of experiment , are found in tables 1-3 .

DISCUSSION

If we consider the CaO/Na_2SiF_6 ratio , it is evident that the lower the ratio than the optimum the less the reaction with NaF , with the result that some free NaF will remain in solution without being transformed to CaF_2 . Contrary to this if the ratio is higher than the optimum , lime will react with sodium silicate in solution and calcium silicate is precipitated. In the first case, we get a lower percentage of fluorine recovered as CaF_2, and a lower percentage of Silica recovered as sodium silicate. The percentage recovery in sodium silicate solution represents the percentage of SiO_2 originally contained in the fluosilicate, which was recovered as Na_2SiO_3 in solution. In the same way, the percentage fluorine recovery represents the percentage of original fluorine in Na_2SiF_6, which was recovered as CaF_2.

It is evident that the purity of calcium fluoride product, depends on the extent of reaction between sodium hydroxide and silicic acid i.e. on the percentage silicate recovery . The conditions were so varied as to get the best quality of calcium fluoride together with best concentration and recovery of sodium silicate solutions.

In table I , the results indicate the effect of CaO/Na_2SiF_6 ratio on the percentage recovery of SiO_2 and F respectively , in dilute solutions . It can be seen that whereas the maximum F recovery is 97.5% , the SiO_2 recovery in the same sample is 53.1%, with a purity of CaF_2 of 83.6% . It is clear that the concentrations of silicate solutions are very low.

In table II the CaO/Na_2SiF_6 was kept constant , while the concentration was varied , within the range of 20 to 100 grams fluosilicate per litre . Results indicate better recovery values for both silicate and fluorine , with increase in concentration . At the same time , better concentrations of silicate solution were achieved .

Table III represents a continuation to table II , where a higher range of concentrations was studied , with a fixed ratio of 1 : 1 . The range of concentrations studied shows good results representing a big improvement especially in the concentrations of silicate solutions. A maximum concentration of about 17% sodium silicate was obtained , with a maximum recovery of 83.3%.In the same run , fluorine recovery was 99.7% , with a product of 86% CaF_2 .

RESULTS

The reactions between sodium silicofluoride and lime for the production of sodium silicate solution and calcium fluoride , were studied for the first time . This preliminary study showed that it is possible to get these products with reasonable specifications . However , we are continuing our efforts to make products with better specifications , especially that matters will be more complicated when commercial lime is used. Our experiments with commercial lime gave rise to a lower grade of calcium fluoride , as all the impurities originally contained in lime , were transferred to calcium fluoride .

Table I

No	Variables				Filterate Na_2SiO_3				SiO_2 Recovery %	Ppt CaF_2				F Recovery %
	Na_2SiF_6 gms	CaO gms	Ratio CaO/Na_2SiF_6	H_2O c.c	Vol. c.c	Conc. °Bé	Na_2O %	SiO_2 %		Weight gms	CaO %	CaF_2 %	F %	
1	20	18.2	0.91	1000	1000	1.3	0.40	0.32	50.0	27.0	58.0	77.9	38.0	84.6
2	20	19.1	0.95	1000	1000	1.4	0.45	0.26	40.6	27.5	59.5	79.13	38.6	87.5
3	20	20.0	1.0	1000	1000	1.6	0.50	0.28	43.7	28.0	60.8	80.0	39.0	90.0
4	20	20.9	1.05	1000	1000	1.8	0.55	0.30	46.9	28.5	61.2	82.0	40.0	94.0
5	20	21.8	1.09	1000	1000	2.0	0.60	0.34	53.1	29.0	62.0	83.6	40.8	97.5

Table II

No	Variables				Filterate Na_2SiO_3				SiO_2	Ppt CaF_2				F
	Na_2SiF_6 gms	CaO gms	Ratio CaO/Na_2SiF_6	H_2O c.c	Vol. c.c	Conc. °Bé	Na_2O %	SiO_2 %	Recovery %	Weight gms	CaO %	CaF_2 %	F %	Recovery %
1	20	20	1.0	1000	1000	1.3	0.4	0.29	45.3	28	59.5	79.5	38.8	89.5
2	40	40	1.0	1000	1000	2.4	0.8	0.9	70.5	58	60.0	80.0	39.0	93.2
3	60	60	1.0	1000	1000	3.0	1.2	1.4	72.9	87	60.5	80.4	39.2	93.7
4	80	80	1.0	1000	1000	4.0	1.6	1.9	74.2	115	61.5	81.0	39.5	93.6
5	100	100	1.0	1000	1000	5.0	2.5	2.4	75.0	145	62.3	81.6	39.8	95.1

Table III

No	Variables				Filterate Na_2SiO_3				SiO_2	Ppt CaF_2				F Recovery
	Na_2SiF_6 gms	CaO gms	Ratio CaO/ Na_2SiF_6	H_2O c.c	Vol. c.c	Conc. °Bé	Na_2O %	SiO_2 %	Recovery %	Weight gms	CaO %	CaF_2 %	F %	%
1	100	100	1.0	1000	1000	5.0	2.6	2.4	75.0	145	62.3	81.6	39.8	95.2
2	150	150	1.0	1000	1000	9.0	3.8	3.7	77.1	218	62.8	82.8	40.4	96.8
3	200	200	1.0	1000	1000	13.0	5.4	5.0	78.1	290	63.2	83.6	40.8	97.5
4	250	250	1.0	1000	1000	17.0	7.8	6.5	81.2	365	64.1	84.7	41.3	99.4
5	300	300	1.0	1000	1000	21.0	9.4	8.0	83.3	432	64.8	86.1	42.0	99.7