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

A NEW FLUORINE RECOVERY PROCESS

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In the manufacture of phosphoric acid by the wet process, fluorine compounds are evolved at various stages. In general they have been largely regarded as a nuisance and scrubbing and neutralisation have been required to prevent stream and atmospheric pollution. The fluorine represents a potential valuable byproduct, but the methods of recovering it from the gases or solutions have not been very attractive economically. This paper describes a new process which permits the economical recovery of a very substantial part of the evolved fluorine in the form of commercial strength hydrofluosilicic acid.

All commercially-used phosphate rocks contain large quantities of fluorine. With the exception of certain ocean island deposits, fluorine content is approximately 3.5 to 4.0%. In the manufacture of 54% P_2O_5 phosphoric acid by the conventional gypsum process, the fluorine distribution and evolution from a typical Florida pebble rock are about as shown in Table 1.

TABLE 1FLUORINE DISTRIBUTION

<u>Source</u>	<u>% of F in Rock</u>	<u>Average lbs. F per ton P_2O_5</u>
Reactor Vapors	4 to 6	12
In Gypsum	18 to 30	58
Evaporator Vapors	35 to 50	101
Evaporated Acid	<u>25 to 35</u>	<u>72</u>
Total	100	243

It can be seen from these figures that a very substantial portion of the fluorine is evolved during the concentration of

the acid.

The process to be described recovers 85-95% of this fluorine as a 15-28% hydro-fluosilicic acid. This process depends on scrubbing the vapors leaving the evaporator under vacuum with a recirculated solution of fluosilicic acid whose temperature is approximately that of the vapors, so that little or no water is condensed, while the SiF_4 and HF are absorbed in the fluosilicic acid solution. The vapors from the recovery scrubber are then totally condensed in the usual barometric condenser ahead of the vacuum system.

Figure No. 1 is a schematic flowsheet of the process. Two plants utilizing this process are in operation in the United States and plants are under construction in Belgium and Germany. The process has created a great deal of interest and several other plants are seriously considering installing this process.

At the two existing plants forced circulation vacuum evaporators are in two and three stages, respectively. Figure No. II is a flowsheet of a three-stage evaporator with fluorine recovery on all three stages. The operating data which follows was obtained at the plant having the three-stage evaporator but before the third stage had been installed. This particular plant is designed to produce 180 short tons per day of P_2O_5 as 54% P_2O_5 phosphoric acid. The evaporator flash chambers are provided with fluorine recovery spray chambers 8.5 feet in diameter. Pilot plant work indicated that vapor velocity in the spray chamber of 12 to 15 feet per second would give satisfactory recovery with three tiers of spray. The figures in Table 2 illustrate how this criteria is met in this particular plant.

Recirculating pumping rate is 500 gpm with 50 psig at the nozzles. All equipment is rubber-lined except the nozzles which are Monel. Table 3 gives some operating data from a series of runs, each of 8 hours' duration. In these runs, continuous samples were taken of the acids, and periodic samples were taken of the vapors by connecting a highly evacuated train to probes in the vapor ducts. Percent recovery is overall, through both stages of evaporation.

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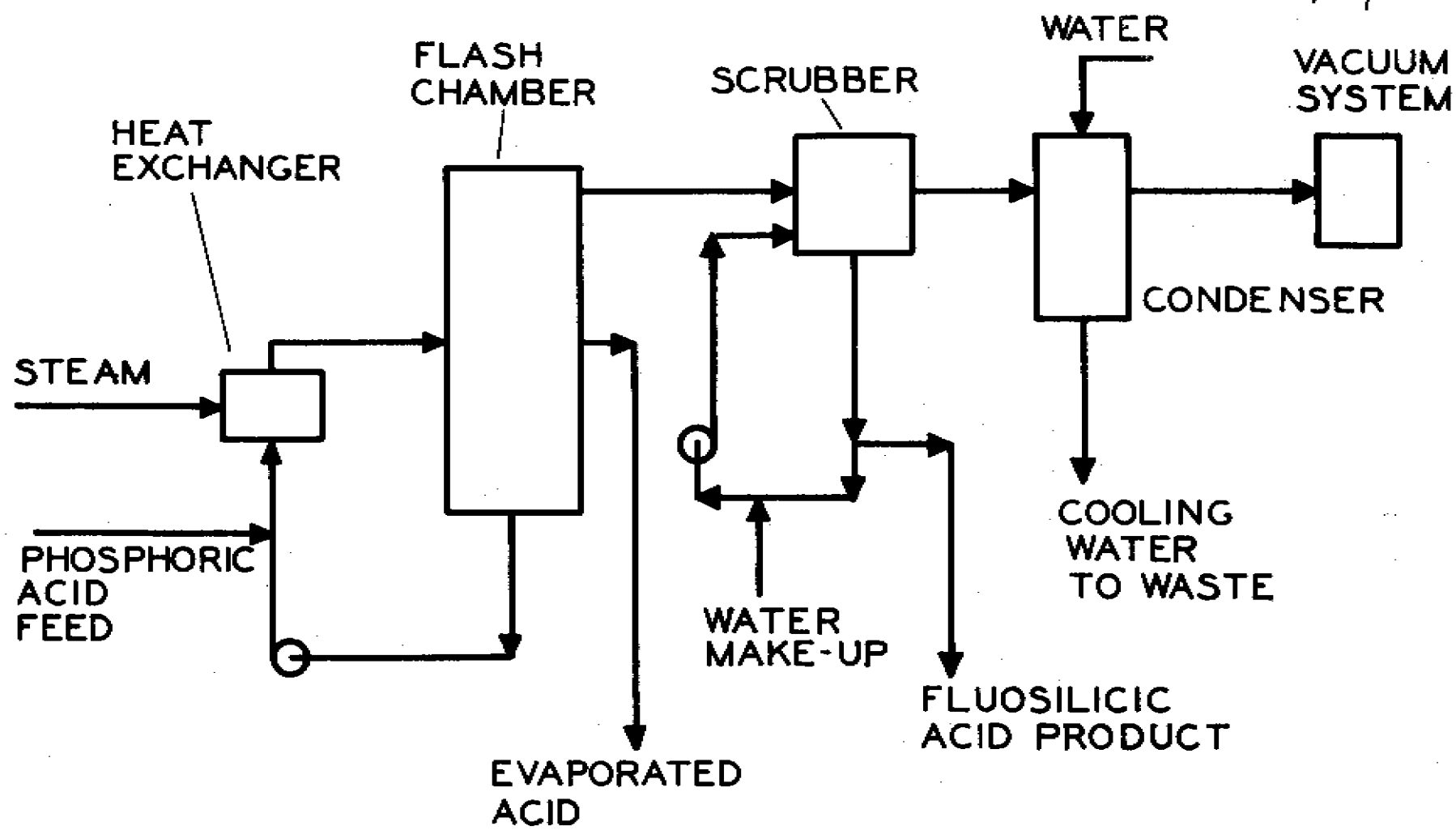


FIGURE I
BASIC FLOWSHEET
FLUORINE RECOVERY SYSTEM

FIGURE II
FLWSHEET - COMMERCIAL INSTALLATION
EVAPORATION WITH FLUORINE RECOVERY

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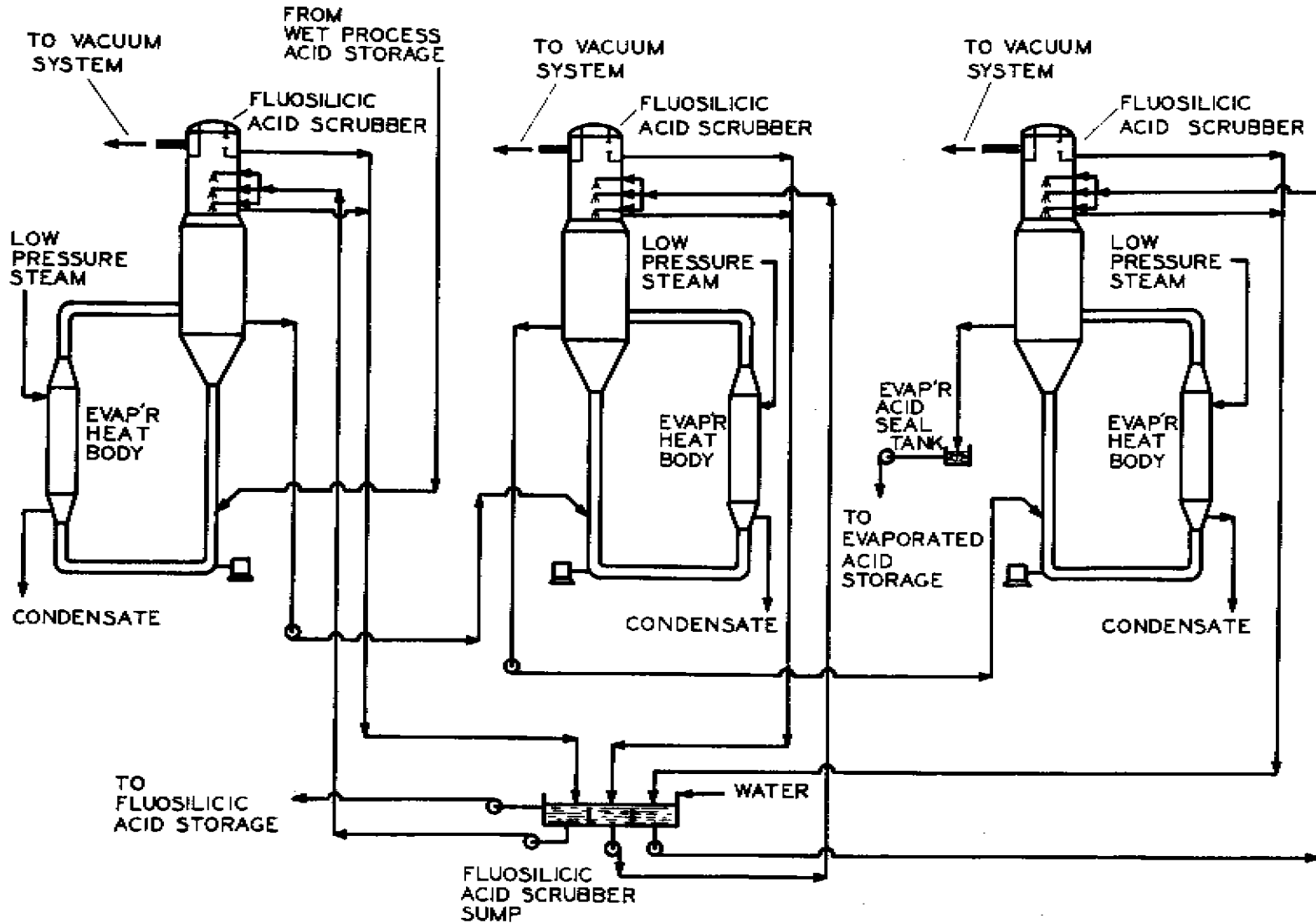


TABLE 2
OPERATING DATA

	<u>1st Stage</u>	<u>2nd Stage</u>
Feed	600 TPD-30% P_2O_5	422 TPD-42.6% P_2O_5
Product	422 " -42.6% "	333 " -54% "
Abs. Pressure	4" Hg.	1.92 " Hg.
Boiling Temp.	70°C	75°C
Evaporation	178 TPD	89 TPD
Specific Volume-vapor	175 c.f./lb.	352 c.f./lb.
C.F.5.	720 "	725
Velocity in Scrubber	12.6 ft/sec.	12.7 ft/sec.

TABLE 3

SWIFT & CO. FLUORINE RECOVERY PROCESS TEST RESULTS

	1	2	3	4	5	6	7
	%	%	%	%	%	%	%
Phos. rock used in making acid. P_2O_5	33.30	33.30	32.20	32.20	32.20	32.20	32.20
F P_2O_5	4.06	4.06	3.80	3.80	3.80	3.80	3.80
H_3PO_4 Feed to 1st Evap. P_2O_5	32.19	30.82	29.27	25.74	26.72	24.34	33.09
F P_2O_5	2.58	2.52	2.98	2.36	2.13	2.27	2.21
H_3PO_4 Feed to 2nd Evap. P_2O_5	46.85	45.02	44.37	45.27	43.20	44.17	42.74
F P_2O_5	2.40	2.35	2.43	2.52	2.28	2.40	2.27
H_3PO_4 Prod. 2nd Stage. P_2O_5	57.85	56.01	54.33	53.78	54.45	54.10	54.91
F P_2O_5	2.09	1.74	1.69	2.02	1.87	1.96	1.58
Vapor from 1st Scrubber F	0.39	0.23	0.54	0.10	0.48	0.31	.98
Vapor to 1st Scrubber F	2.54	2.31	2.58	0.83	2.05	2.34	1.84
Vapor from 2nd Scrubber F	.08	.06	0.26	0.20	.22	.09	1.05
Vapor to 2nd Scrubber F	4.54	4.80	2.96	4.78	3.86	3.26	5.49
Fluosilicic Acid Product % H_2SiF_6	27.01	25.80	28.32	17.95	29.77	22.69	33.20
Efficiency of Recovery H_2SiF_6	88.5	93.0	83.0	92.5	84.5	90.5	68.0
H_3PO_4 Feed Rate to 1st Stage GPM			98	70	83	91	70

1st Stage Evaporator operated at
3.8 to 4.9 in absolute Hg. 73° to 81°C
2nd Stage Evaporator Operated at
1.3 to 2.4 in absolute Hg. 79° to 82°C

Table 4 gives the fluorine recovery expressed as pounds of fluorine per ton of P₂O₅ through the evaporators.

TABLE 4.
FLUORINE RECOVERED PER TON P₂O₅ IN FEED

Run	%F Feed	%H ₂ SiF ₆ Product	% F Recov.	Lbs. F T P ₂ O ₅
1	2.58	27.01	88.5	78
2	2.52	25.80	93.0	94
3	2.98	28.32	83.0	118
4	2.36	17.95	92.5	100
5	2.13	29.77	84.5	76
6	2.27	22.69	90.5	104

Avg. lbs. F recovered per
ton P₂O₅ to Evap. 95

There has been no difficulty with silica scaling or deposition. The final composite acid is substantially free of any suspended silica. Apparently since the fluorine is present in the phosphoric acid as hydrofluosilicic acid or metal fluosilicates, these decompose and are evolved as follows:



and in the scrubber the gases are hydrated and the fluorine compounds re-combined:



In the first stages there is apparently a preferential evolution of SiF₄ and there may be some free silica in the recovered acid, but in the final stages, there is a preponderant evolution of HF so that the combined acids do not contain excess or free silica.

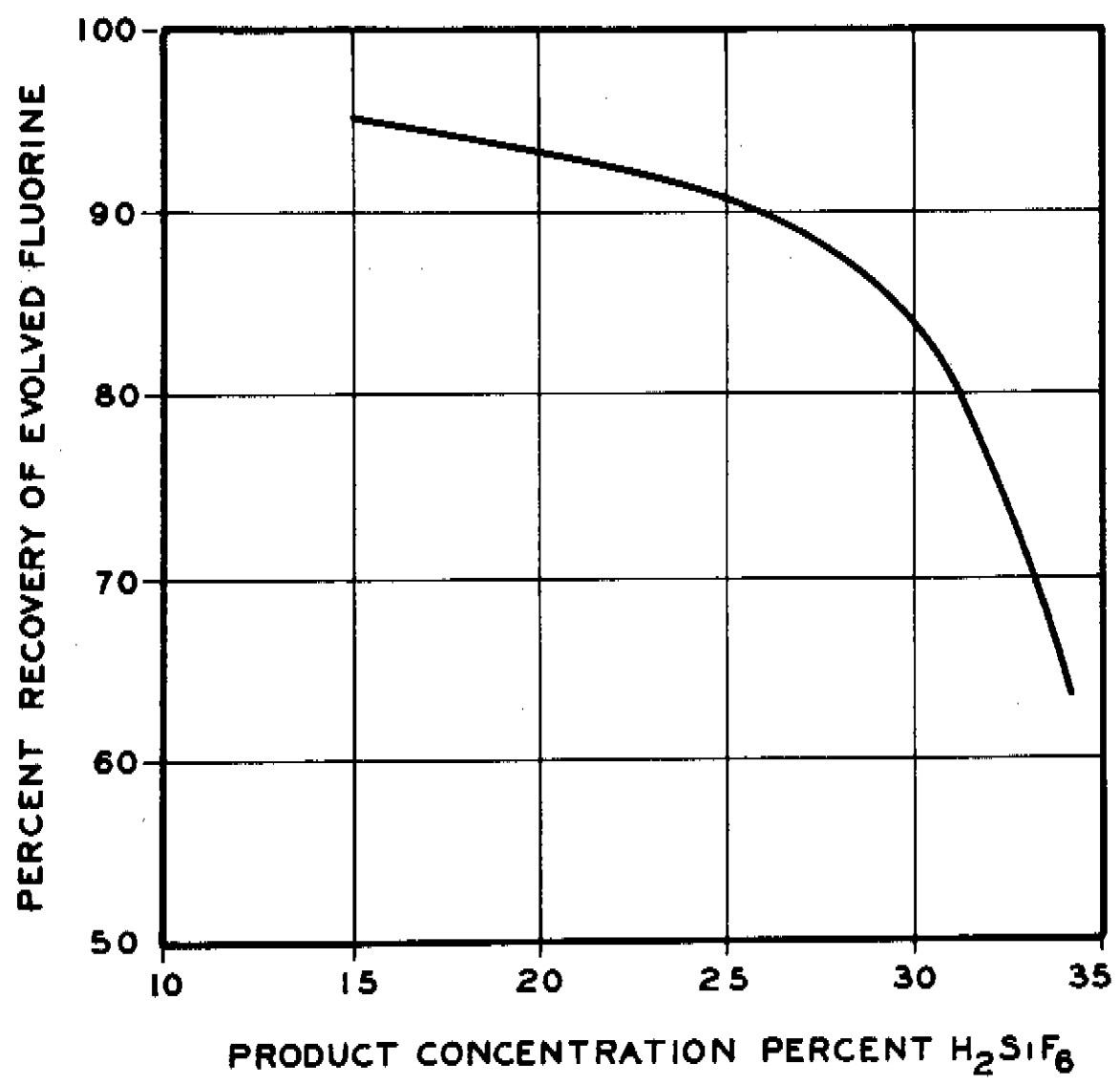
The recovery efficiency, as a function of hydrofluosilicic acid strength, has been plotted in Figure No. III.

The process described herein has been in successful operation for two years in one plant and for ten months in another.

25% hydrofluosilicic acid is finding increasing acceptance

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FIGURE III
EFFECT OF PRODUCT CONCENTRATION
ON
FLUORINE RECOVERY



as a fluoridating agent for public water supplies in the United States, and much of the production from these two plants finds its way into that market. The remainder of the production is processed with sodium chloride into sodium silicofluoride of 99.5% purity, which finds a ready market also for water fluoridation, as well as in the ceramic and glass industries.

This process is covered by U.S. patents issued and pending, and applications for patents have been filed in the major industrial countries in the world. The plants have been designed and supplied by the Dorr-Oliver Companies.

DISCUSSION

Mr. W.C. WEBER (U.S.A.) : This paper deals with a process for recovering the fluorine evolved in the manufacture of wet process phosphoric acid. The fluorine compounds evolved in the various stages of this manufacture have, in the past, been regarded as a nuisance, requiring innocuous disposal. The recovery method described in the paper recovers a great deal of this fluorine as a commercial strength hydrofluosilicic acid.

On page 1 of the paper, we give a distribution of the fluorine evolution in a typical plant using Florida rock. This distribution varies very considerably with different types of rock. With Florida rock, over 40% of the fluorine content is evolved in the vapour from the evaporators when concentrating to 54% P_2O_5 . The evolution is, of course, less with a lower concentration.

The process described recovers about 85-95% of the fluorine in the vapours from the evaporators. The recovery is inversely proportional to the strength of the acid produced. One can obtain recoveries in this range when making a 15-20% solution of hydrofluosilicic acid. The process is very simple : the vapours leaving the flash chamber of the vacuum evaporator are scrubbed under vacuum with a solution of fluosilicic acid, the temperature of which is approximately that of the vapours. Thus, little or no water is condensed, whilst the SiF_4 and the hydrofluoric acid are absorbed in the fluosilicic acid solution. The lean vapours from the fluorine scrubber are then passed to the usual barometric condenser for total condensation and disposal, and there is, of course, a vacuum pump. A specific gravity controller actuates a valve which discharges the hydrofluosilicic acid to storage when up to the desired strength. Make-up water flows into the hot wall through a float-control valve. In this way, we obtain a quite uniform solution.

The process is in operation at three phosphoric acid plants. Figures are given in the paper, and there is a reference to two of these plants; but we recently put one into operation in Belgium. The two described in the paper are in the U.S.A. One of them is a two-stage evaporator, and the other is a three stage evaporator.

In the two-stage operation, the phosphoric acid is concentrated from about 30% P_2O_5 to 42% in the first stage; and from 42% to 54% in the second stage. It is interesting that the silica tetrafluoride is apparently volatilized more rapidly than its stoichiometric equivalent of hydrofluoric acid. There is, therefore, an excess of SiO_2 in the first stage scrubber; and an excess of HF in the second stage. Silica precipitation is prevented in the first stage by using overflow from the second stage scrubber hot well as make-up for the first and by adding all make-up water to the second stage circuit. The product - hydrofluosilicic acid - is overflowed from the first stage. When producing a final product of 25% hydrofluosilicic acid, the recirculating liquid is held at approximately 12% - 15% in the second stage scrubber.

The efficiency curve is of interest: it shows that we have made up to 33% - 34% hydrofluosilicic acid at a loss in recovery; but that we can get 85% recovery with 30% acid or less. Most of the plants in the U.S.A. run at about 25% - the strength used for the fluoridation of water. The two plants in the U.S.A. using this process sell their hydrofluosilicic acid as such for the fluoridation of water and for the production of sodium silicofluoride.

This process was developed by Swift & Co., and I am sorry Dr. Sanders could not be here. He did the pilot plant work, and the two installations are in Swift plants, from which we obtained the data.

Mr. F.P. MENDES (Portugal): This paper is an interesting contribution on the subject of the recovery of an important fraction of a by-product with an increasing commercial value. Although a certain quantity of fluorine remains in the acid, even after concentration, this is not important, as the main purpose is the production of phosphoric acid.

At the last ISMA Technical Conference in Wiesbaden, Mr. Breeze, of Fisons, presented a paper on the recovery of fluorine as a by-product of superphosphate manufacture. I should like to know Mr. Weber's opinion as to the most suitable way to recover fluorine - during the acid manufacture, or during subsequent concentration?

Secondly, I should like Mr. Weber to say whether the temperature control of the circulated solution of fluosilicic acid

is obtained by the addition of make-up water or by any other device.

Thirdly, from an examination of the results of Test 4, there seems to be a direct relationship between the concentration of the phosphoric acid feed to the first evaporator and the concentration of the fluosilicic acid obtained. Could Mr. Weber comment?

Mr. WEBER : The question as to which is the better method of fluorine recovery, either by mixing the sulphuric and phosphoric acids and thus obtaining a rather strong fluorine evolution, as put forward by Mr. Breeze in his previous paper, or by adopting the method described in my paper, may depend on the type of phosphate rock used and the extent to which the phosphoric acid is being concentrated, and several other considerations. If you have a market for the fluorine - and this, of course, is the big problem - you can recover the fluorine evolved in the phosphoric acid reaction, as well as that evolved during evaporation. Whilst you will by the mixing, or stripper, method, increase the amount of fluorine liberated during the reaction, there will still be a considerable quantity remaining in the strong acid which will evolve during evaporation.

In this respect, I have some figures relating to the fluorine distribution. Table 1, in our paper, gave this distribution for a typical Florida rock, and even then we have to give a rather considerable range. There seems to be a great number of various factors affecting this distribution. We recently compiled some data from three plants using Morocco phosphate rock, and in this case the fluorine distribution is very different. We had 17% - 31% of the fluorine being evolved in the reaction, whereas with Florida rock we obtain only 5% - 10% at most. Also with the Morocco rock, there is much less fluorine in the strong acid. However, this is partly offset by the fact that we get a much more complete evolution of the fluorine during evaporation with the Morocco rock. As a result, whereas with Florida rock, concentrating to 54%, we have about 1.5% to 2% fluorine in the 54% acid, with Morocco rock the corresponding figure is only 0.3% to 0.5%. Consequently we find that with the latter 20% to 40% of the fluorine in the rock is evolved in the evaporator when concentrating to 54% acid, with only 4% - 8% of the fluorine remaining in the acid, as compared to 25% - 35% in Florida acid.

What this would appear to indicate in relation to Mr. Mendes' question is that there would be a great deal more incentive in the case of Morocco rock to recover the fluorine during the reaction, because there is so much more of it. With Florida rock, there is so little evolved during the reaction that it is hardly worth recovering it, although it has to be scrubbed out to meet atmospheric pollution restrictions. But we can very nicely combine the scrubbing of the gases from the reactor with the fluorine scrubber on the evaporator, because we can produce a weak solution from scrubbing the reactor gases and use it as make-up in the evaporator circuit.

The second question related to temperature control. There is no temperature control required, because the recirculated hydrofluosilicic acid automatically attains the same temperature as the vapours rising from the evaporator. The latter are, of course, controlled by a vacuum control in the evaporator.

With regard to the fact that Test 4 seemed to show that the concentration of fluosilicic acid produced was a function of the phosphoric acid feed concentration, I think this is just an experimental error. We have not found any correlation of this sort, and I would not expect theoretically that there would be.

Mr. N.D. GOPINATH (India) : Would Mr. Weber indicate the impurities present in the hydrofluosilicic acid which is used in the fluoridation of water, especially impurities such as P_2O_5 and silica?

Secondly, the paper states that the methods of recovering fluorine from the gases or solutions have not been very attractive economically. Does this mean only in respect of hydrofluosilicic acid in the U.S.A., or does it apply generally. In India, we import large amounts of synthetic cryolite and are considering manufacturing it ourselves in order to restrict the imports. The recovery of fluorine from the stack gases of the superphosphate process and from the obnoxious vapour condensers in the phosphoric acid plant is to be combined, and a plan has been put forward for the recovery of 1 ton/day of synthetic cryolite. One plant is already working in India, producing 15% hydrofluosilicic acid. We have estimated that, bearing in mind our expansion plans, we shall be in a position to

manufacture roughly 5 tons/day of synthetic cryolite from the superphosphate and phosphoric acid plant gases alone. The cost of installation works out at about \$60,000. The present price of synthetic cryolite in India is about \$200 per ton, and our cost of production comes to about \$150 per ton. The proposition is thus economical.

Mr. WEBER : With regard to the impurities in the hydrofluosilicic acid, I cannot give the exact figures, but in these evaporators the entrainment loss is about 0.2% - 0.3% of the P_2O_5 fed in, and this would be removed in the hydrofluosilicic acid. But we have not found it objectionably high for either water fluoridation or sodium silicofluoride production, but we have no experience with other compounds.

With a 54% phosphoric acid, the fluorine-silica ratio seems to be almost exactly that corresponding to H_2SiF_6 . We end up with a clear solution of hydrofluosilicic acid, although there might be a slight excess of HF at times. However, if you concentrate to some intermediate level, you would have an excess of silica. As I pointed out, in a two- or three-stage evaporator, the first stage may be quite cloudy with precipitated silica. The second stage will be only slightly affected and the third stage will usually be clear, if you concentrate to as much as 54%; but if you evaporate to only 40% - 45% you would probably have some silica in suspension. If you want to remove it, you would have to filter it off, and, in this case, it would be better to do it in the scrubber circuit.

The point I made regarding recovery of the fluorine from the reaction vapours was that, in the case of plants operating on Florida rocks, the amount evolved was hardly enough to bother about, when you can obtain so much in the way described in the paper. But with Morocco rock, and also certain other rocks, giving heavy evolution, it would obviously be quite economical to recover the fluorine in the reaction fumes.