International
Fertilizer Industry
Association

ISMA* Technical Conference

The Hague, The Netherlands
13-16 September 1976

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

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PROCESS FOR RECYCLING H_2SiF_6 SOLUTIONS RECOVERED BY GAS WASHING, TO THE DEN OF SUPERPHOSPHATE

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1) TECHNOLOGY OF THE RECYCLE OF FLUORINE

1.1) Use of fluorine

The technology of the production of superphosphate is too well known to make a description necessary.

In the last few years the always increased interest both in the ecological and economical aspect, has made further developments on such technology necessary.

It is known that the gaseous effluents from the den, generally contain 20 ÷ 30% of the fluorine in the phosphate rock; such gases are scrubbed in empty towers in which water is fed so as to obtain a solution of H_2SiF_6 with silica in suspension. The fluosilicic acid solution obtained usually contains 20 ÷ 28% of H_2SiF_6 and so 16 ÷ 22% of F.

Many minor producers discard the solution directly; other more conscientious producers neutralize it before discarding.

Major producers such as Montedison, are equipped with a centralized plant for the recovery of fluorine in which the solutions coming from the scattered superphosphate plants are fed. Doing so it is possible to obtain by-products such as sodium fluoride, sodium fluosilicate etc..

Such recovery of fluorine is in many cases not economic and besides the problem of the disposal of silica which contains fluorine, P_2O_5 etc. is unavoidable.

To overcome these difficulties, and to use the H_2SiF_6 solution in the same superphosphate plant more conveniently, the Fertilizer Research Center of Montedison has developed a technology that allows a reduction of the fluorine content in the stack gases and an utilization of H_2SiF_6, together with the sulphuric acid, to attack the phosphate rock in the production of superphosphate.

1.2) Process description

There are the following operating sections:

a) The phosphate rock is brought into contact, with sulphuric and the H_2SiF_6 solution coming from the following sections by means of a mechanical mixer.

b) The mixture from section a) falls into the den where the reaction continues at a temperature varying from 100° to 115°C.

c) Gases and water vapour evolved from the den are fed into scrubbing towers in which water is also added to produce acid containing 20 ÷ 28% H_2SiF_6 and silica. This slurry is recycled into section a).

d) The product from the den goes to curing and afterwards it may be granulated.

A flow diagram of the plant is shown in fig. 1.

A schematic arrangement of the chemical reactions concerning the recycled H_2SiF_6, is as follows:

$$2\ H_2SiF_6 + Ca_3(PO_4)_2 + 2H_2O = 2CaSiF_6 2H_2O + Ca(H_2PO_4)_2 \quad (1)$$

$$CaSiF_6 2H_2O + 2H_2O = CaF_2 SiO_2 2H_2O + 4HF \quad (2)$$

$$4HF + Ca_3(PO_4)_2 = 2CaF_2 + Ca(H_2PO_4)_2 \quad (3)$$

The reactions show that every mole of reacting H_2SiF_6 corresponds to three moles of H_2SO_4. As a result it is necessary to lower the ratios of H_2SO_4 and water in respect to the phosphate rock.

1.3) Results of industrial tests

In table 1 the working conditions of two Montedison plants are shown in detail.

In the first plant, equipped with a rubber belt type den, Land Pebble rock is used whilst in the second plant, equipped with a rotary drum type den, Morocco Khouribga rock is used. Table 1 underlines the differences between the traditional operation and the operation with a fluorine recycle.

It can be seen that, for both rocks, the fluorine recycle leads to a reduction in the H_2SO_4 consumption of about 20 kg per ton of produced superphosphate. The H_2O/rock ratio remains unaltered in respect to the traditional process, and it is consequently necessary to increase the H_2SO_4 concentration to balance the water introduced with H_2SiF_6. Retention time in the den, and therefore the plant capacity, is not changed by the H_2SiF_6 recycle.

The analyses of the produced superphosphate in the four conditions are shown in table 2.

It can be seen that the H_2SiF_6 recycle causes a lowering in the grade of the superphosphate of about 0.2 points of available P_2O_5. If this lowering in concentration is not acceptable, it is necessary to increase again the concentration of H_2SO_4 or the one of the recycled H_2SiF_6.

By recycling H_2SiF_6 to the superphosphate den, a F/P_2O_5 ratio equal to the one of the initial phosphate is obtained: this means that all the fluorine in the phosphate rock remains fixed in the superphosphate. The chemical characteristics of the superphosphate do not deteriorate because water soluble F content remains at the same level of the superphosphate's obtained without the H_2SiF_6 recycle. In fact, as it can be seen

BLE 1 - Operating conditions

QUANTITIES	Units of measure	Without H_2SiF_6 recycle		With H_2SiF_6 recycle	
		Land Pebble	Khouribga	Land Pebble	Khouribga
		A	B	C	D
1. Ground phosphate rock					
1.1 Chemical analysis					
Water	%W	1.2	0.7	1.2	0.7
P_2O_5	″	33.1	32.6	33.1	32.6
CaO	″	48.5	51.4	48.5	51.4
CO_2	″	4.0	4.2	4.0	4.2
SO_4	″	1.2	2.0	1.2	2.0
F	″	3.8	4.1	3.8	4.1
SiO_2	″	3.4	3.0	3.4	3.0
F/P_2O_5	″	0.115	0.126	0.115	0.126
1.2 Screen analysis					
+ 0,150 mm	%W	6.5	11.0	7.0	11.4
0,150 ÷ 0,075 mm	″	38.5	37.5	37.6	37.9
- 0,075 mm	″	55.0	51.5	55.4	50.7
2. Operating conditions					
2.1 Acid: Rock Ratio					
Rock/Superphosphate	kg/t	562	572	556	566
H_2SO_4 100%/Superphosphate	″		372	350	352
H_2SiF_6 100%/Superphosphate	″	-	-	18.6	21.7
SO_4 from H_2SO_4/P_2O_5 total	″	1.94	1.95	1.86	1.87
2.2 Acids concentrations					
H_2SO_4	%W	67.5	66.7	75.3	74.5
H_2SiF_6	″	-	-	23.3	25.5

TABLE 1 - Second part

QUANTITIES	Units of measure	Without H_2SiF_6 recycle		With H_2SiF_6 recycle	
		Land Pebble	Khouribga	Land Pebble	Khouribga
		A	B	C	D
2.3 Introduced water					
H_2O/Rock	kg/kg	0.316	0.325	0.315	0.325
2.4 Den:					
Type	-	belt conveyor	drum	belt conveyor	drum
rotational speed	r.p.m.	-	0.79	-	0.79
linear speed	m/min	1.30	-	1.30	-
inclination	degrees	-	9	-	9
holding time	min	24	16	24	16
traduction rate	t/day	900	800	900	800
2.5 Temperatures					
H_2SO_4	°C	47	40	46	40
H_2SiF_6	"	-	-	60	60
Exit mixer	"	82	78	85	81
Exit den	"	104	100	105	100

TABLE 2 - Analysis of the produced superphosphate

QUANTITIES	Units of measure	Without H_2SiF_6 recycle		With H_2SiF_6 recycle	
		Land Pebble	Khouribga	Land Pebble	Khouribga
		A	B	C	D
1. Superphosphate after 24 h					
Water	%W	12.3	12.0	12.1	11.8
water soluble P_2O_5	"	16.1	16.7	15.8	16.8
available P_2O_5	"	17.3	17.8	17.0	17.6
insoluble P_2O_5	"	1.2	0.8	1.3	0.8
total P_2O_5	"	18.5	18.6	18.3	18.4
water soluble F	"	0.5	0.6	0.5	0.65
total F	"	1.59	1.75	2.11	2.3
total F/total P_2O_5	-	0.086	0.094	0.115	0.125
attack yield	%	93.5	95.7	92.9	95.7
2. Superphosphate after 10 days					
Water	%W	11.8	11.5	11.6	11.4
water soluble P_2O_5	"	17.1	17.4	16.9	17.4
available P_2O_5	"	18.4	18.5	18.2	18.3
insoluble P_2O_5	"	0.2	0.2	0.2	0.2
total P_2O_5	"	18.6	18.7	18.4	18.5
water soluble F	"	0.5	0.6	0.5	0.6
total F	"	1.6	1.76	2.12	2.32
total F/total P_2O_5	-	0.086	0.094	0.115	0.125
attack yield	%	98.9	98.9	98.9	98.9

from reaction (3) the recycled fluorine is transformed into CaF_2.

Also the curing time in the storage building does not change, and after ten days the product has the same mechanical and physical characteristics as the traditional one and it is perfectly suited for utilization.

Table 3 shows the distribution of fluorine in the different sections of a production and granulation plant.

2) PLANTS ARRANGEMENT

2.1) Objectives and reasons

The necessity of arranging the existing plants for the fluorine recycle rises essentially by the following facts:

- In a traditional plant the evolved fluorine in the gas phase is 20 ÷ 30% of the fluorine content in the phosphate rock.

- When the fluorine, in the form of fluosilicic acid, and silica are recycled to the attack section, the flow-rate of evolved fluorine is roughly trebled. With a Morocco phosphate the rate increases from 30 kg of F/t P_2O_5 to 90 kg of F/t P_2O_5.

This increase in loading the fluorine recovery section, can cause some troubles in relation to the pollution of the flue gases.

There are the following laws in Italy concerning air pollution:

- The 1972 Collective Agreement for workers in the chemical Industry states that the maximum concentration allowed in the air in the working area is 3 ppm (expressed as F).

- The law concerning air pollution states that in every point, outside the factory perimeter the concentration of the fluorine compounds must be less than 0,02 mg/m^3. As a result, some measures both on an industrial plant and on laboratory scale, have been carried out, to draw the elements for the design of the new scrubbing sections.

The traditional scrubbing plants are formed essentially of empty towers in which a circulating solution of fluosilic acid is sprayed. The introduction of grids in the towers allows an increase in their performances.

The above measures were put into practice with the aim of finding out the increase in the towers effectiviness induced by the grids and their life to the silica clogging. Laboratory measures have shown the vapour pressure of fluorine in the field of low concentration as required by the cited laws.

2.2) Results of laboratory work

The vapour pressure of fluorine above the H_2SiF_6 solutions is affected by the F/SiO_2 ratio in the liquid phase owing to the different evaporating compounds. The diagram of fig. 2, taken from literature data, shows the HF/SiF_4 ratio in the vapour phase in equilibrium with H_2SiF_6 solutions at different silica contents.

The HF and SiF_4 have different volatilities. As a result the silica content affects the F/H_2O ratio in the vapour phase: this is shown in fig. 3.

The laboratory measurements were carried out therefore with silica in excess to reproduce the industrial scrubbing plant conditions. Measurements were performed with the dynamic method proposed by A.L. Whynes (Trans. Instn. Chem. Engr. Vol. 34 1956).

The results are shown in the diagram in fig. 4.

2.3) Plant measurements

Measurements were carried out putting Moplen (polypropylene) grids into an empty sprayed tower to evaluate the grids effect. This evaluation is done in terms of mass transfer coefficients by means of the well known equation:

$$\ln \frac{y_1 - y^*}{y_2 - y^*} = \frac{k_g\, a\, z}{\omega} \qquad (4)$$

in which:

$y_1 ; y_2 ; y^*$ = gas phase fluorine concentration at the tower inlet, at the tower exit and at the equilibrium respectively

k_g = mass transfer coefficient

a = specific gas-liquid contact surface

z = tower height

ω = gas phase rate

The towers were equipped with sets of sprayers every 3 meters of the height according to the fact that short towers have a higher efficiency per unit volume than tall ones. The grids spacings are about 1 cm. The liquid feed rate was constant at the value of 5000 ÷ 6000 liters.m^{-2}.h^{-1}.

It is however known that the tower efficiency is strongly dependent on the liquid feed-rate and there is a dependence of $k_g a$ from L of the following type:

$k_g a = \alpha L$

where α is a constant and L is the liquid feed rate.

The results of our measurements, expressed in terms of $k_g a$ with the aid of equation (4) and the vapour pressure of fig. 4, are shown in the diagram of fig. 5.

It can be seen from 5 that a dependence of $k_g a$ from of the type $k_g a = BL\, \omega^{0,8}$ supported by previous published data is confirmed, when B is another constant.

The grids supplied tower, has a mass transfer coefficient roughly three times higher than the one of the empty tower. As a result of the arrangements of the scrubbing section the fluorine emission to the stack is reduced when compared with the traditional operation, as can also be seen in table 3.

A long length test showed that in the grid-supplied tower, with a fluorine concentration in the gas up to 600 mg/m^3, disturbing silica cloggings were not found.

3) CONCLUSIONS

The advantages that can be obtained with the proposed process are of two kinds:

- In respect to the ecological concern:

a) removal of the pollution connected with the discard of the solid and liquid by-products;

b) reduction of the air pollution

- Economic advantages

a) The residue disposal costs are eliminated (dirty silica)

b) The liabilities of the possible conversion of fluosilicic acid into technical fluorides are avoided

c) Reduced sulphuric acid consumption to produce superphosphate

d) The superphosphate plants become independent from the market situation of the fluorine compounds.

The new features of the fluorine recycle superphosphate plant in respect to traditional plants are:

- Connection between the H_2SiF_6 tank and the raw material mixer.

- Insertion of grids in the fluorine scrubbing towers to increase their efficiency.

These new features can easily be adapted to every existing traditional plant and even more so in the design of new plants.

BLE 3 - Fluorine distribution

QUANTITIES	Units of measure	Without H_2SiF_6 recycle		With H_2SiF_6 recycle	
		Land Pebble	Khouribga	Land Pebble	Khouribga
		A	B	C	D
1. Fluorine in the rock	kg/h	800.8	780.9	795.1	772.7
2. Fluorine in the superphosphate	"	600.0	586.1	794.8	772.4
3. Fluorine at the exit of the den	"	200.8	194.8	552.3	572.2
4. Fluorine at the exit of the first tower	"	20.0	20.0	120.0	120.0
5. Recovered and recycle fluorine	"	200.3	194.3	552.0	571.9
6. Fluorine in the stack gases	"	0.5	0.5	0.3	0.3
7. Evolved fluorine from granulation (*)	"	1.2	1.2	1.2	1.2
8. Evolved fluorine from drying (*)	"	40	43	45	49
9. Fluorine in the most polluted air of the plant	mg/m^3	0.34	0.34	0.23	0.23

(*) The fluorine is scrubbed in a suitable section with lime and recycled in the granulation section

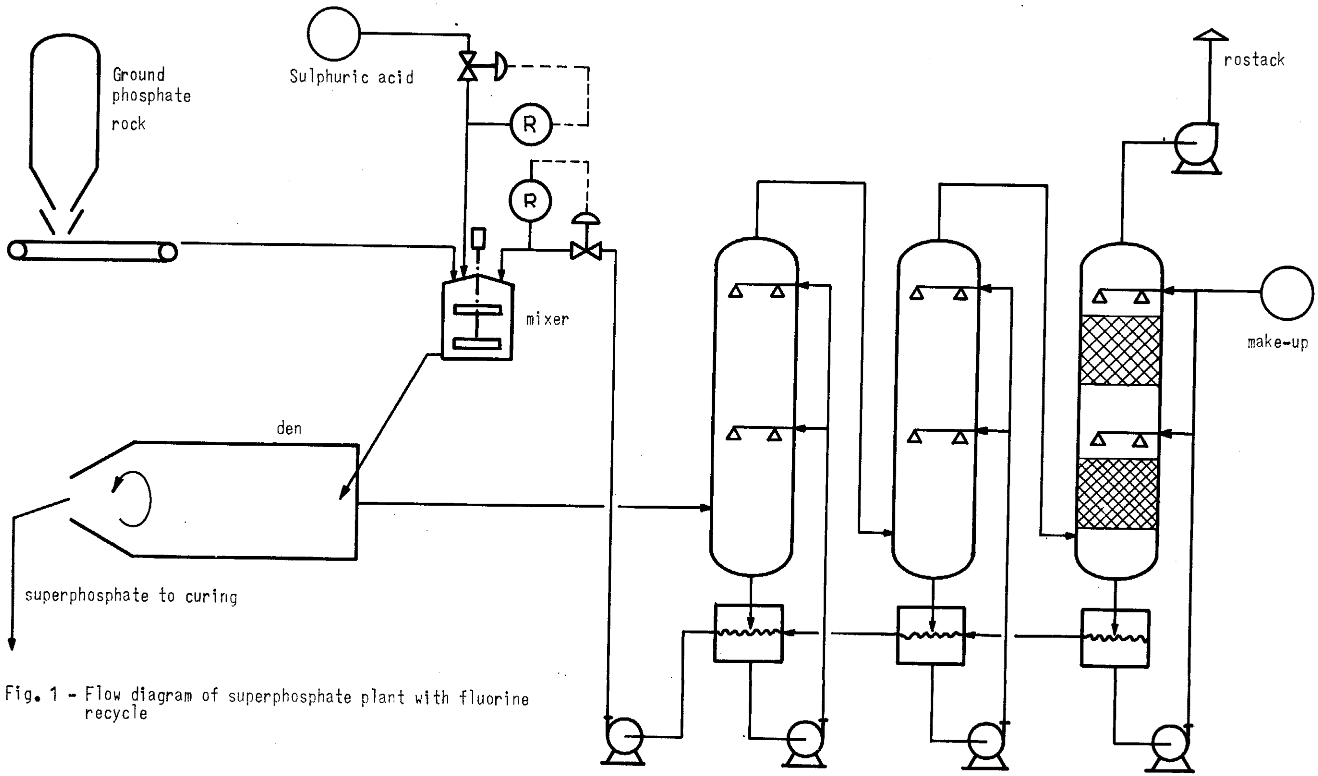

Fig. 1 - Flow diagram of superphosphate plant with fluorine recycle

Source: Z.G. Smirnova Issled. Obl. Neorg. Tekhnol. "Nauka" Leningrad 1972 pag. 202-209

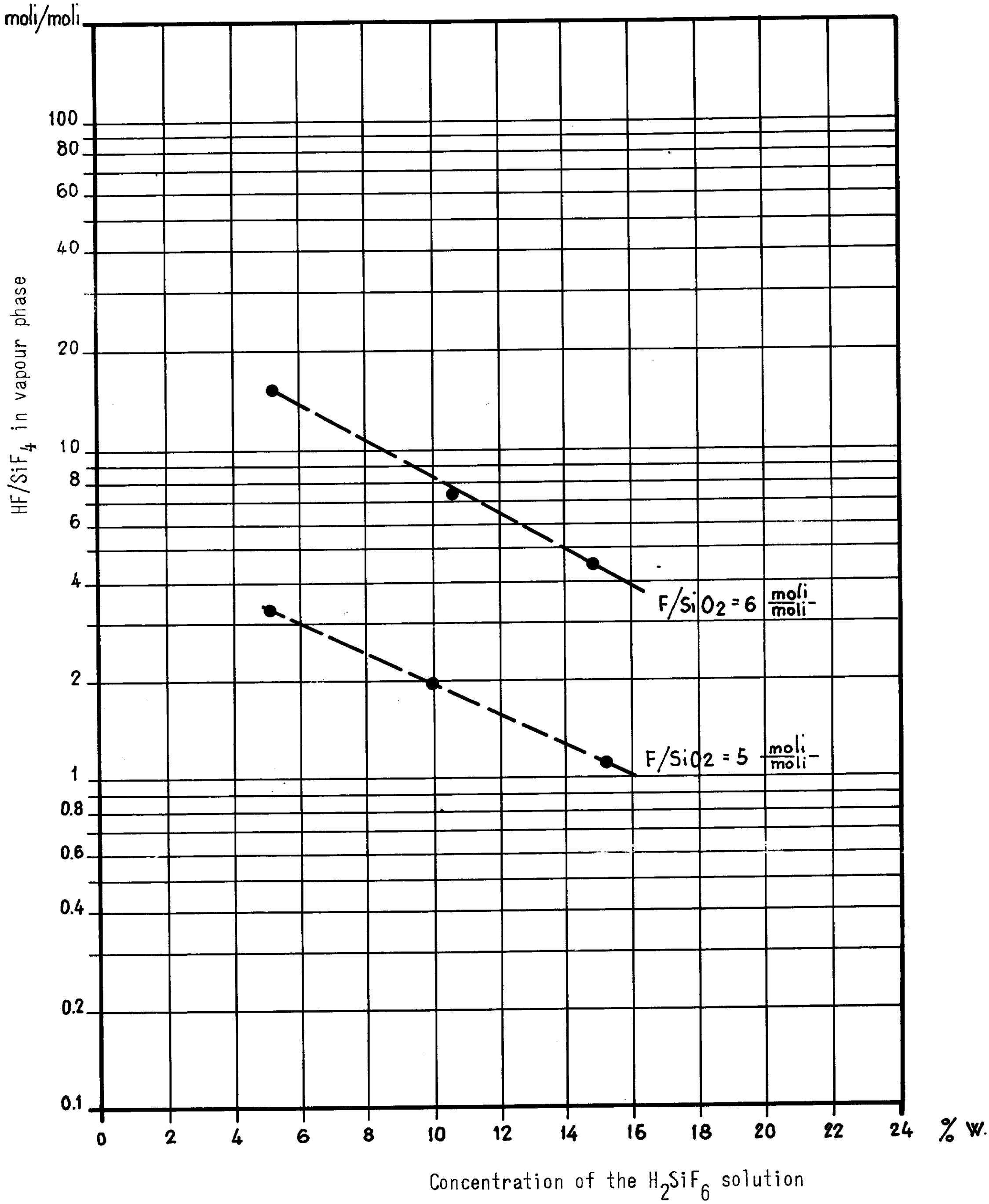

Fig. 2 - HF/SiF_4 ratio in the vapour phase in equil. with H_2SiF_6 solution for different silica contents

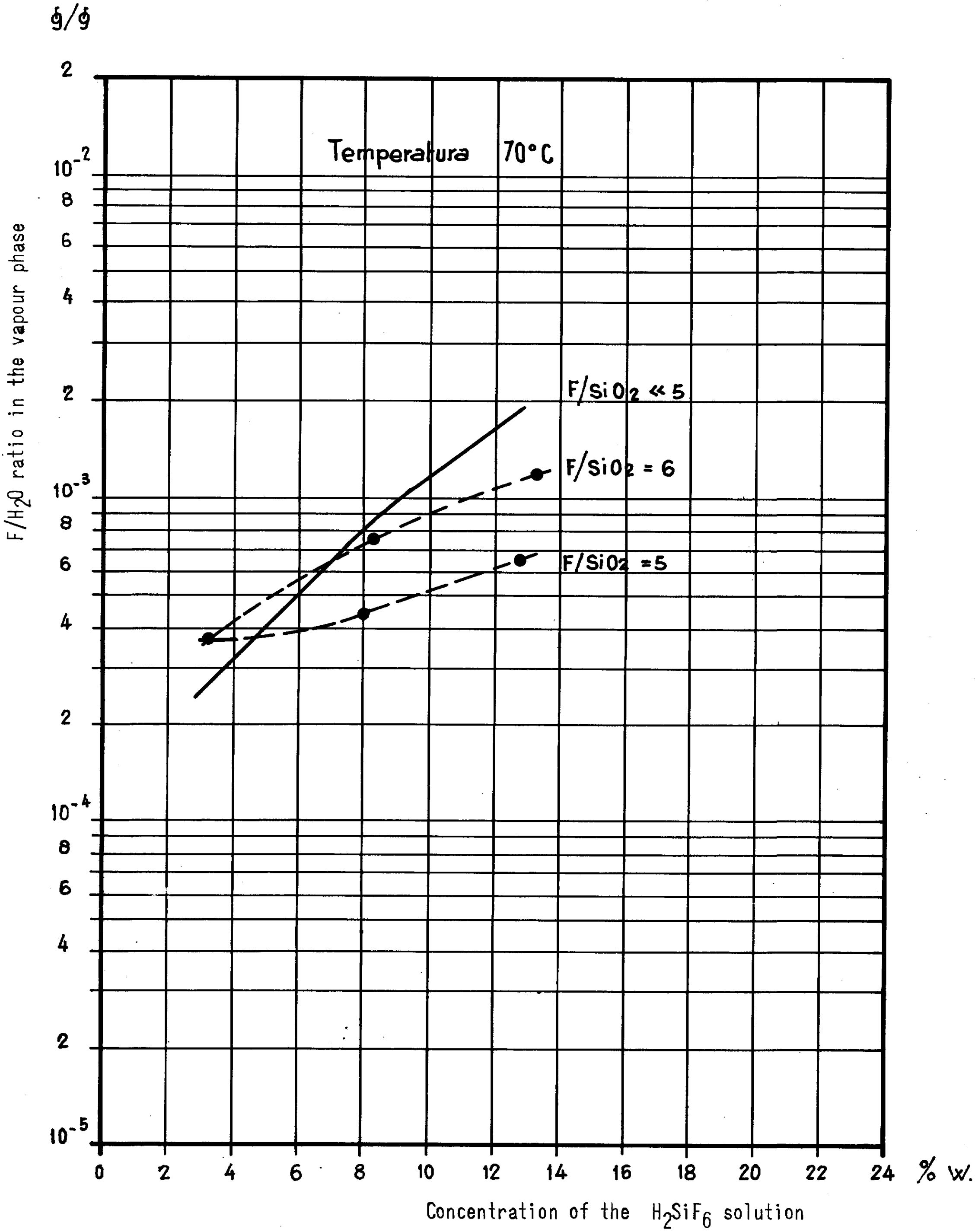

Fig. 3 - F/H_2O ratio in vapour phase in equilibrium with H_2SiF_6 solution for different silica contents

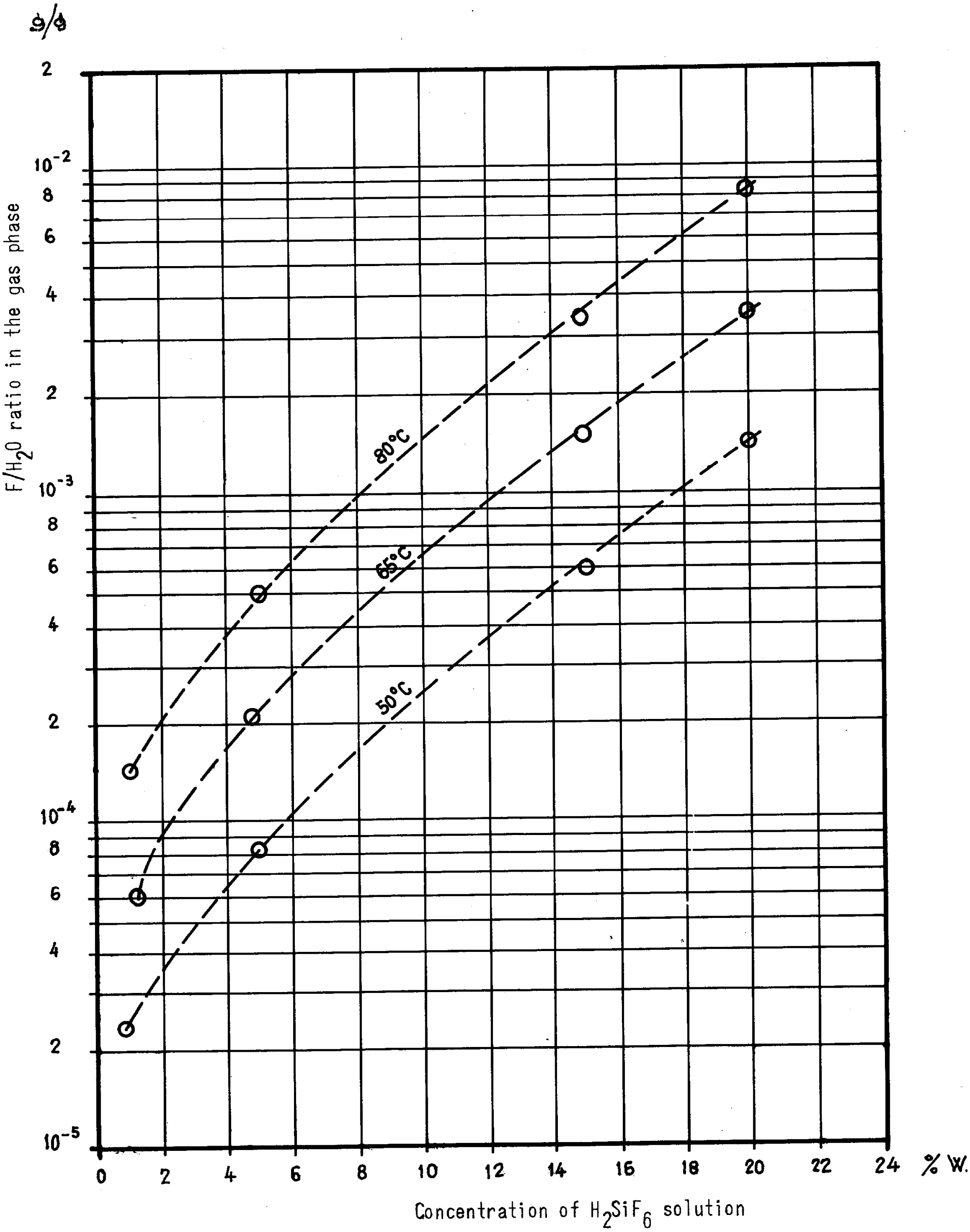

Fig. 4 - Gas phase composition in equilibrium with H_2SiF_6 solution and silica ($F/SiO_2 \ll 5$)

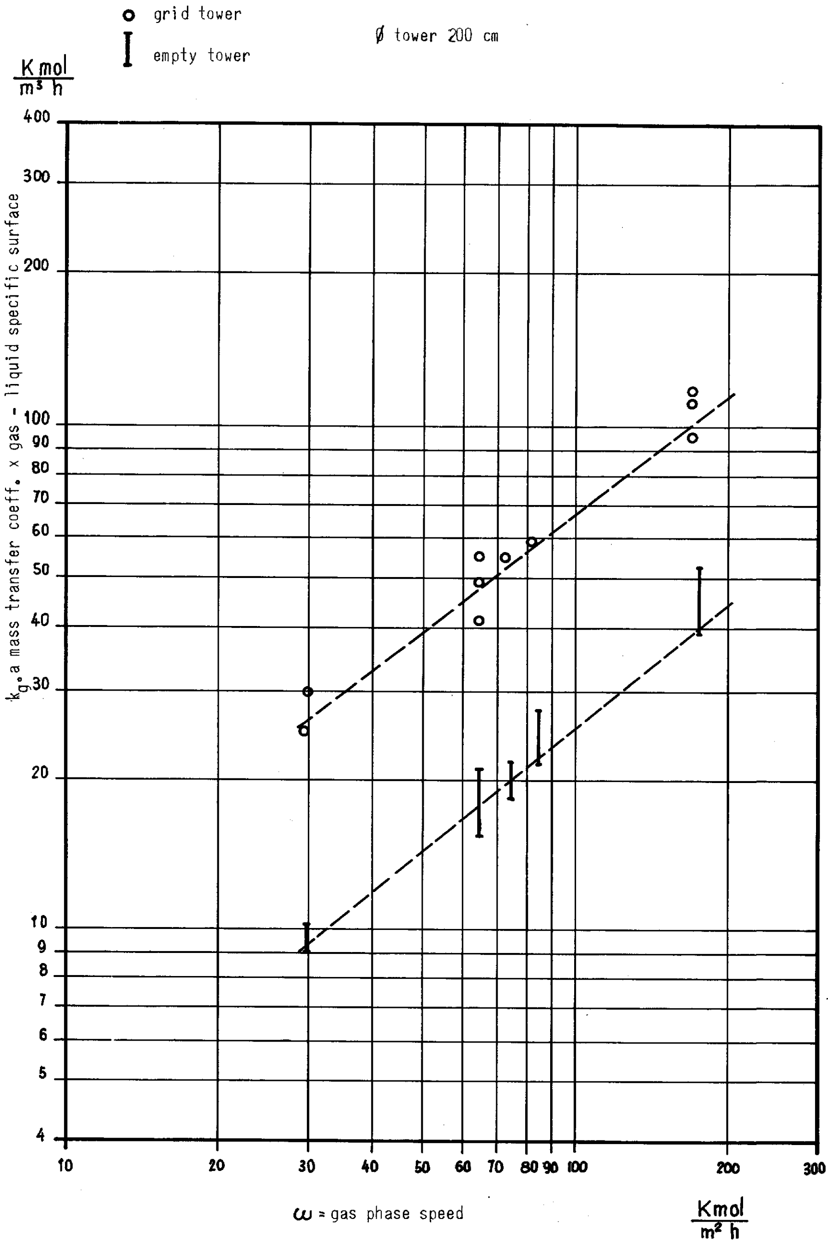
o grid tower
empty tower
Ø tower 200 cm
Kmol / m³ h
k_g. a mass transfer coeff. x gas - liquid specific surface
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
10
20
30
40
50
60
70
80
90
100
200
300
ω = gas phase speed
Kmol / m² h

Fig. 5