ISMA* Technical Conference

Seville, Spain
20-24 November 1972

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

# ROTATING DISC TOWERS FOR SiF$_4$ ABSORPTION

By

G Menin and G B Guarise
Fabbrica Perfosfati Cerea;
Universita di Padova, Italy.

The removal of fluorine compounds present in the exhaust gases from the continuous superphosphate acidulation process, is of increasing importance in restricting air pollution.

The new Italian law on air pollution control imposes very severe limits on the fluorine content in the air around industrial perimeters: 0.06 ppm as peak concentration and 0.02 ppm as average concentration (by volume). In order to keep the fluorine content within the above range, the concentration at the chimney, it is thought, must be below 50 ppm. This made us redesign our scrubbing plant, the performance of which has been described in a previous paper [6].

GASES EVOLVED IN THE SUPERPHOSPHATE ACIDULATION PROCESS

The reactions giving off gaseous fluorine compounds during the acidulation process are not yet completely understood. According to SEMRAU [4] the gases produced are thought to contain mainly SiF$_4$ and the reactions can be simplified as follows:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\ HF \qquad (1)$$

$$4\ HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O \qquad (2)$$
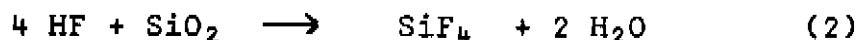
Delomenie [2] and Whynes and Dee [8] actually demonstrated that the quantity of SiO$_2$ and silicates present in the phosphate rocks is sufficient to complete the reaction (2).

The factors affecting the amount of SiF$_4$ in the gases produced are:-

a. concentration and temperature of the used H$_2$SO$_4$;

b. size of the ground phosphate rock;

c. fluorine content in the phosphate rock.

The SiF$_4$ concentration is also a function of the suction rate of the gases out of the den.

The effect of the size of the ground phosphate rock
on the amount of fluorine given off in respect of the
total amount of fluorine present in the phosphate rock,
X_F, is shown in Figure 1.

While Delomenie and Whynes and Dee's values are from
Morocco phosphate rocks, ours are from a mixture of
Taiba 80/82 BPL and Gafsa 65 BPL phosphate rocks with
about 4 per cent F and 1.7 per cent CO_2 by weight.

This behaviour can be explained taking into account the
fact that with phosphate rocks very finely ground the
chemical attack is extremely fast and the life of the
fluid phase of the reactants is very short. Conse-
quently the acid concentration decreases very rapidly
reducing the flourine given off, as the above factor
a. suggests. This also justifies the negligible effect
of the residence time in the den on the amount of evolved
fluorine: variations up to 30 per cent of the residence
time are not noticeable from the amount of fluorine
given off.

The gases sucked out of the Kuhlmann den are mainly air,
H_2O, CO_2 and SiF_4. The suction is applied at the be-
ginning and at the end of the den (see Figure 2).

Table 1 gives the composition of the gases at two points
in the den. The CO_2 has been evaluated with the obvious
hypothesis that all the CO_2 from the phosphate rocks is
collected at point 1. The H_2O amount has been found by
absorption in concentrated H_2SO_4.

TABLE 1

Composition of the Sucked Gases at the Beginning

and at the End of the Den. These Values Refer to

a Production of about 11 ton/h of Single

Superphosphate

|	point 1				point 2			
	H_2O	CO_2	SiF_4	air	H_2O	CO_2	SiF_4	air
F (g/m³ at the meter)	100	34	8.3 (°)	1125	49	–	1.1 (°)	1125
per cent molar	12.3	1.7	0.24	85.7	6.7	–	0.04	93.3

(°) value given in g of fluorine per m³ of gas

The fluorine was measured in the .01 N NaOH solution
from the three absorbers through which 100 litres of
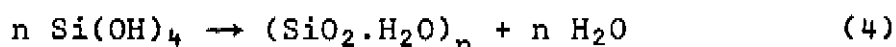sampling gas was passed. The sampling flow rate was of

about 60 litres per hour, measured with a volumetric flowmeter. The fluorine concentration was measured potentiometrically with a selective LaF_3 electrode.

Scrubbing Plant

a. <u>SiF Absorption in Water</u>: SiF_4 can be easily hydrolised to silicic and fluosilicic acids, according to the following reaction:

$$3 \; SiF_4 + 4 \; H_2O \longrightarrow Si(OH)_4 + 2 \; H_2SiF_6 \qquad (3)$$
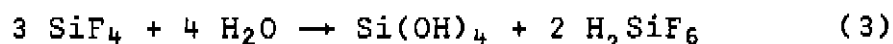
The silicic acid can then polymerize as follows:

$$n \; Si(OH)_4 \longrightarrow (SiO_2.H_2O)_n + n \; H_2O \qquad (4)$$

giving rise to a colloidal suspension that, concentrated, results in the formation of a gel.

Whynes ([8], [9]) noticed that water drops exposed to an air flow containing SiF_4 were very rapidly covered by a silica layer that inhibited any further absorption. Whynes' results have been obtained at a partial pressure of SiF_4 of 80 mmHg, but a similar behaviour cannot be excluded even at the much lower partial pressure in the scrubbing plants, as reported by Sherwin ([7]), Calver and Hemsley ([1]). The $Si(OH)_4$ certainly formed on the drop surface, alters the absorbing surface and might hinder the diffusion of H_2SiF_6 to the internal part of the drop, precluding the renewal of the surface even at a very low partial pressure of SiF_4.

From Whynes' data the vapour pressure of SiF_4 on H_2SiF_6 solutions turns out to be extremely low for temperature and acid concentration up to $70^\circ C$ and 0.2 respectively. This shows how very easy it is to absorb SiF_4 in water; nevertheless the following conditions should be fulfilled:

A - frequent renewal of the liquid surface;

B - easy removal of solid SiO_2.

It is obvious that these conditions cannot be fulfilled in a packing tower; therefore jet scrubbers and spray towers are preferred.

We found that the rotating disc towers are particularly suitable for fulfilling the above conditions; condition A specially is obtained in a more efficient way than with jet scrubbers or spray towers.

The first rotating disc towers plant was installed in 1952 ([5]); the two towers were of ebonite covered.

steel and the gases, coming from the two ends of the den, were treated separately. Each tower was followed by a fan with an interposed cyclone, necessary to stop the droplets that would otherwise consistently reduce the scrubbing efficiency.

The improvements introduced into the new plant are substantially concerned with the design, the building material and the easier shape of the rotating discs.

b. Scheme Choice: The values of fluorine concentration at the two suction points (see Table 1) suggested modifying the original design (5, 6), the second tower being oversized. The scheme of Figure 3 was therefore chosen.

The plant is prearranged for the insertion of a further cyclone after the fan: this has been suggested by the operating conditions; in fact droplets and mist formation is very probable; in addition the fan can become a supplementary scrubber injecting the fan wheel with water.

c. Construction Details: The two towers rest on a re-inforced concrete tank covered with bricks, with a proof layer in between; the lid is made of a moulded concrete plate. Two hydrolic guards close the bottom of the towers, and the liquid level is kept constant by a weir.

The gases coming from the first tower join those sucked from the end of the den and pass through the second tower, that is followed by the cyclone and the fan (6,300 m^3/h at 200 mmH_2O) driven by a 10 HP electrical motor. The two suction flow rates are of 4,500 and 1,700 m^3/h respectively; these values can slightly increase with the production rate of the den. Figure 3 shows also that an auxiliary fan can be used.

Fresh water is introduced over the first disc of the 2nd tower: the flow rate can be varied between 40 and 100 litres/minute, 35 l/min. being the normal value at which all the experimental values given in this paper have been taken.

A submerged pump at the bottom of the second tower recycles the solution into the first tower; the flow rate is about 300 ÷ 350 l/min.

The plant is all polypropylene constructed, apart from the fan wheel; the rotating shaft of the towers is made of iron and covered with a thick polypropylene pipe supporting seven discs. The shaft rotates at about 310 rev/min and is suspended at the top and simply

guided at the bottom of the towers.

The towers consist of three sections. Each tower contains seven discs and six conical liquid redistributors. Each disc can be inspected through large rectangular windows that facilitate the periodical cleaning operations.

Some initial difficulties, particularly in manufacturing the flanges, was surmounted. Special care was devoted to the problem of the strong thermal expansion of polypropylene, with specific regard to the different expansions of the thick polypropylene pipe supporting the discs and the iron shaft.

The shaft rotation has been limited to about 300 rev/min both to avoid too hard a strain for the shaft and because every further increase does not improve noticeably the scrubbing efficiency. Similar behaviour was found by Heertjes in the distillation field; he found that the efficiency was constant above 200 rev/min ([3]).

The tower diameter, 1,200 mm, gives a reasonable gas velocity of 1.7 ÷ 1.8 m/sec (empty tower). In the tower the gas velocity actually changes continuously up to 5 ÷ 6 m/sec.

In Figure 5 are shown the drops turbulence and dispersion obtained between two discs. A picture of the plant is given in Figure 6.

Plant Efficiency

Let us consider a rotating disc as a stage of the counter-current absorption process. In the case of fresh water feed, $x_1 = 0$ (x = mole fraction of SiF_4 in the liquid), the working line is according to the equation:

$$y_{n+1} = y_o + \frac{L}{G} x_n \qquad (5)$$

y = mole fraction of SiF_4 in the gas;

L, G = molar liquid and gas flow rates;

i, o = subscripts for inlet and outlet conditions.

Equation (5) applies to the section below the n-th stage (numbered starting from the top).

Strictly speaking the variations of the flow rates, particularly G, should be taken into account. These variations are slightly due to the absorbed SiF_4 and CO_2, but mainly to the H_2O condensation. Nevertheless, for the

sake of simplicity, the gas is thought to consist only
of air; this criterion has also been adopted by Sherwin.

Let us consider now the stage efficiency according to
the well known Murphree formulation:

$$E_M = \frac{y_{n+1} - y_n}{y_{n+1} - y^o_n} \qquad (6)$$

y^o_n = vapour composition at equilibrium with the liquid
of composition x_n.

In our case, since the ponderal fraction of H_2SiF_6 in
the liquid is certainly less than .2, y^o_n can be taken
equal to zero. From equations (5) and (6) applied to
the total N stages it follows:

$$\frac{y_o}{y_i} = (1 - E_M)^N \qquad (7)$$

It can be easily verified that equation (7) holds for
$x_i \neq 0$ too, i.e., for the tower No.1 with solution re-
circulation. Equation (7) obviously implies E_M to be
constant along the tower.

The first measurements taken at points 1, 2, 3, and
4 (see Figure 3) have given the mean values of Table 2.

TABLE 2

Fluorine Content at the Points of Fig.3

	phosphate rocks 3 Ton/h				phosphate rocks 6.5 Ton/h			
	P mmH$_2$O	T °C	F (g/m³ sucked)	ppm SiF$_4$	P mmH$_2$O	T °C	F (g/m³ sucked)	ppm SiF$_4$
point 1	-15	56	3.9	1,200	-15	72	8.3	2,410
point 2	-10	42	0.4	128	-10	60	1.1	400
point 3	-50	40	0.3	93	-50	56	0.8	230
point 4	0	35	0.04	12	0	46	0.07	20

From these values the efficiency E_M for the two towers is
derived by equation (7) and shown in Table 3. In the same
Table, the specific absorption capacity K_ga is also re-
ported, as it can be evaluated by the following correlation:

$$\ln \frac{y_i}{y_o} = \frac{K_g a V \pi}{G} \qquad (8)$$

K_g = total mass transfer coefficient referred to gaseous phase, $Kmole/hm^2$ atm;

a = area of the gas-liquid interface per unit volume, m^2/m^3;

V = tower volume, m^3;

π = pressure, atm;

G = overall gas flow rate, Kmole/h.

It may be pointed out that the efficiencies of the two towers are of the same order, 0.3; a value that is high for an absorption stage. Heertjes, in the work already mentioned ([3]), found a similar value in the benzene-toluene distillation.

TABLE 3

E_M and $K_g a$ Values for the two Towers

The volume V has been computed from

the Discs Number and the Tower Volume

Between two Discs

Phosphate rocks Ton/h	E_M		$K_g a$	
	3.0	6.5	3.0	6.5
tower No.1	0.31	0.29	120	109
tower No.2	0.27	0.31	148	184

The total efficiencies, namely the absorbed fluorine fractions, for the two working conditions are 98.7 per cent and 99.0 per cent respectively.

Conclusions

In Table 4 the characteristic parameters of the rotating disc tower are compared with those of other plants; these latter are taken from Sherwin data.

TABLE 4

Characteristic Parameters of Different

Scrubbing Plants

	spray towers	packed towers	jet scrubbers	rotating disc towers	
Stages in series	2	3	2	2	
$(y_i - y_o)/y_i$	0.99	0.931	0.987	0.991	
S (m^2)	2.43	0.74	0.23	1.13	
V (m^3)	25.7	10.25	3.42	3.5 + 3.5	
G' $(m^3 h^{-1})$	2,040	5,100	5,100	4,600	6,300
L' $(m^3 h^{-1})$	3.5	8.2	82	19	3.3
L $(Kmole\ h^{-1} m^{-2})$	40	307	19,700	935	162
$K_g a$ $(Kmole\ h^{-1} m^{-3} atm^{-1})$	16.6	59	250	109	184
$K_g a/L$ $(m^{-1} atm^{-1})$	0.416	0.193	0.0127	0.117	1.14
V/G' $(h\ .\ 10^3)$	12.6	2.1	0.67	1.1	

The absorption rate per unit volume for rotating disc towers is noticeably higher in respect of spray and packed towers. Taking into account also the liquid flow rate, the comparison is substantially favourable for the discs tower in terms of $K_g a/L$.

With regard to the volume of tower space necessary for the unit's gas flow, only a jet scrubber requires less; a packed tower needs almost twice the volume while a spray tower will be nearly ten times larger.

We believe that the good performance obtained can be improved both by decreasing the suction at the point 2 and by inserting a second cyclone after the fan. Further but probably less notable improvements can be obtained by increasing the water flow rate.

References

(1) Calver, A G and Hemsley, J D C, The Fertiliser Society, London, Proc. No.63 (1960).

(2) Delomenie, H, ISMA Technical Meeting, LE 610, Aarhus (1955).

(3) Heertjes, P M, International Symposium on
    Distillation, Brighton, 189 (1960).

(4) Kohl, A L and Riesenfeld, F C, Gas Purification,
    McGraw Hill Co. New York, 171 (1960)

(5) Menin, A, Brevet Francais, No.1.076.475 (1953)

(6) Menin, G and Guarise G B, Atti Instituto Veneto
    SS. LL. AA., CXXVIII (1969-70).

(7) Sherwin, K A, ISMA Technical Meeting, LE 414,
    Cambridge (1953); Trans Inst. Chem. Engrs, 32,
    129 (1954) Supplement.

(8) Whynes, A L and Dee, T P, ISMA Technical Meeting,
    LE 389, Cambridge (1953).

(9) Whynes, A L, Trans. Inst. Chem. Engrs, 34, 117 (1956).

DISCUSSION

Slides were shown during Mr. Menin's presentation.

MR. G. MENIN (Fabbrica Perfosfati Cerea, Italy):
I have little to add to the paper itself and would like
to show you some slides.

1.   A general view of the installation.

2.   Closer view of part of the plant.

3.   The rotating disc tower.

4.   The dispersion of droplets during operation of
      the tower.

5.   Another view of good droplet dispersion.

6.   Good dispersion of droplets in the gas flow.

As for the paper itself, we have taken it that
the fluorine content at the flue should not exceed
50 ppm.   This limit was calculated from the formula
of Bosante and Pierson under the most common conditions
at the plant site.   In fact, this figure is of the
same order of 0.4 kg/hour of fluorine authorised by
the Dutch authorities.   I think, in any case, that
we can summarise the paper by saying that the
absorption of SiF_4 is very easy provided that the
liquid surface is frequently renewed and that the
solid silica is easily removed.   We feel that the
rotating disc tower can achieve these conditions quite
successfully, and the first 18 months of operation
confirm this.

As to yield, we confess that a total yield of
more than 99% surprised even us and we took care to
check several times before confirming it.

MR. J. M. LOPEZ AZCONA (s.a. Cros, Spain):
The paper by Menin and Guarise describes a type of
rotating disc tower for fluorine absorption and, from
their work, we see that it has clear advantages over
installations designed for this purpose and based on
similar principles.

These include, for instance, the "Knecht"
rotating disc scrubbing towers with internal motors
for driving each disc whereas this type has an
external motor.   We all know the very great problems
which result from having machines in corrosive
surroundings.   The installation is made entirely of
propylene and to make towers of this sort of
propylene or polyethylene is, in our view, to use

the best material.   Those built of ebonite covered
steel give rise to innumerable problems such as
those with hydraulic seals etc.   The constructional
details are good and the efficiency of the system
of rotating disc towers described is very good
according to the figures given in the paper.
It is in general better than other methods
currently employed such as spray, ejector, etc.

I say "in general" because it seems that Bayer,
and, in the superphosphate industry, companies like
ÖSW, GIULINI and GUANO, are carrying out successful
trials on the absorption of residual gases with
silicon tetrafluoride in two simple appliances
placed in series, whose dimensions are 4 x 2.1
with few mechanical parts, operating usually
with a counter-current of water and with part of
the suspension being bypassed to a filter in order
to separate the silica.   A fluosilicic acid is
obtained with an Si/F ratio of 1/5.3 to 1/5.5.
Its simplicity makes it attractive.

One point of criticism is that the
scrubbing water contains only 2% F.   This makes me
think that Mr. Menin's system is acceptable if its
only purpose is to absorb the silicon tetrafluoride
from the escape gases generated in superphosphate
manufacture in order to prevent atmospheric pollution.

The author is fully aware of the high demand
for fluorine compounds both in organic and inorganic
industry (plastics, aerosols, extraction of uranium,
production of aluminium etc.) and the importance in
every process of the economic factor.   This prompts
my question: could the fluorine content of the acid
obtained be raised? In order to obtain a fluo-
silicic acid usable in the aluminium industry we
would need a content of 8 to 9% fluorine, provided
it did not entail a higher content in P_2O_5 than 0.01
(180 ppm in 25% acid) as this would reduce electrical
efficiency. We could thus obtain aluminium fluoride or
fluoride or cryolite, so necessary in the aluminium
industry.

In extreme cases, even if the figures of 8 to
9% quoted were not obtained it would be possible to
reach 2.5-3%. which would enable us, for instance,
to make synthetic fluorspar with a content of, for
instance, 5-6% silica, and obtain pellets for the
metallurgical industry, where a higher phosphorus
content is moreover not a disadvantage.   This would
add a further economic advantage to the achievement
of pollution control.

MR. MENIN: First of all I should like to thank
Mr. Lopez Azcona for his comments, and in answering
them I want to stress the fact that the main purpose
of the installation is the reduction of air pollution.
Another consideration which must be borne in mind is
the small size of the installation itself, i.e. the
small quantities of fluorine recovered in the form of
fluosilicic acid. At all events, six months ago we
began to reduce the amount of fresh water to 15 litres/
minute by recycling the solution in the second tower.
The concentration of the fluosilicic acid increased
under these new operating conditions to 3.4%, at which
level recovery of approximately 88% of the
fluorine from the fluosilicic acid was quite possible.
We think the quantity of water can be further reduced
so as to achieve a concentration of up to about 10%.
In this case a heat exchanger would be fitted to cool
the liquid recycled in the second tower. Neutralisa-
tion of the acid with soda will allow for recovery of
about 95% of the fluorine. The sodium fluosilicate
obtained now is reasonably pure. It is in fact a
little richer in fluorine than in theory it should
be, but this is a question not directly linked to the
argument in the paper. At all events, we estimate
that it is not feasible to recover more than 95% and
that the P_2O_5 content of the sodium fluosilicate is
not enriched. It has been quite low enough for it
to be sold. This recovery is in any case sufficient
to settle the question of liquid effluents, which in
Italy are not allowed to exceed a fluorine compound
content of 10 ppm fluorine. Finally, on the subject
of the cost of the process of neutralising fluo-
silicic acid with caustic soda, I feel that one
cannot speak in terms of profitability when dealing
with the reduction of pollution. It is sufficient,
I think, to recover the operating and investment
costs.

MR. F. ZANETTI (Montedison, Italy): In table 4,
you make a comparison between the various systems of
treating gases with SiF_4. Considering the volume of
the tower, we see for instance that the rotating
disc·tower comes out much better than the spray or
filling tower and is equal to the jet scrubber.
What can you tell us about the consumption of
energy as compared with these various other gas
treatment systems?

MR. MENIN: I apologise, but to reply properly
to these questions I should need a blackboard, since
I think that the one way of representing the operating

characteristics of this installation is Lunde's
diagram, where the number of exchange units is
related to installed power.   At all events, I can
tell you that in this diagram the relative position
of rotating disc towers is about the same as that
of jet scrubbers.   That is to say the power
employed in this system is of the same order as that
employed in jet scrubbers.   In particular, I can
say that we have 5.5 CV per $1,000^3$ metre with an
exchange unit number of 4.8, i.e. virtually the same
results as for the jet towers.
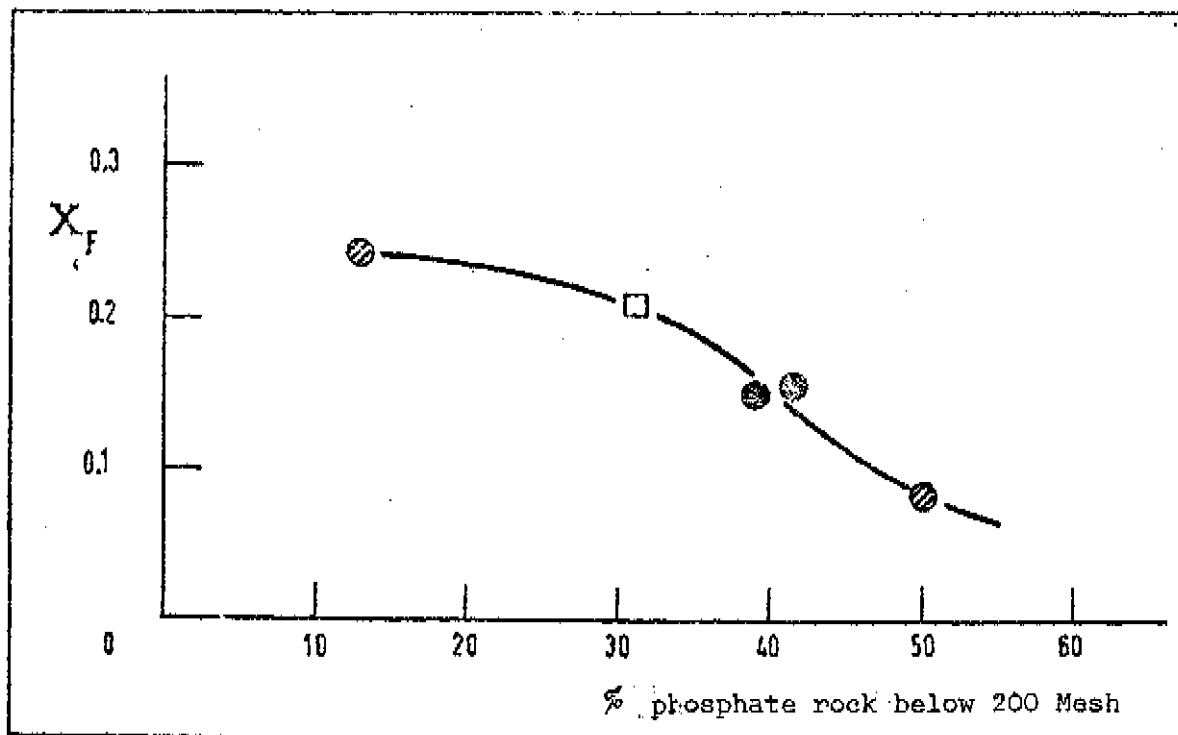
Figure. 1 — FRACTION OF THE TOTAL FLUORINE EVOLVED IN THE
ACIDULATION PROCESS OF PHOSPHATE ROCK WITH
H_2SO_4 70% BY WEIGHT

◉ Delomenie ; ☐ Whynes et Dee ; ◉ Our measurements
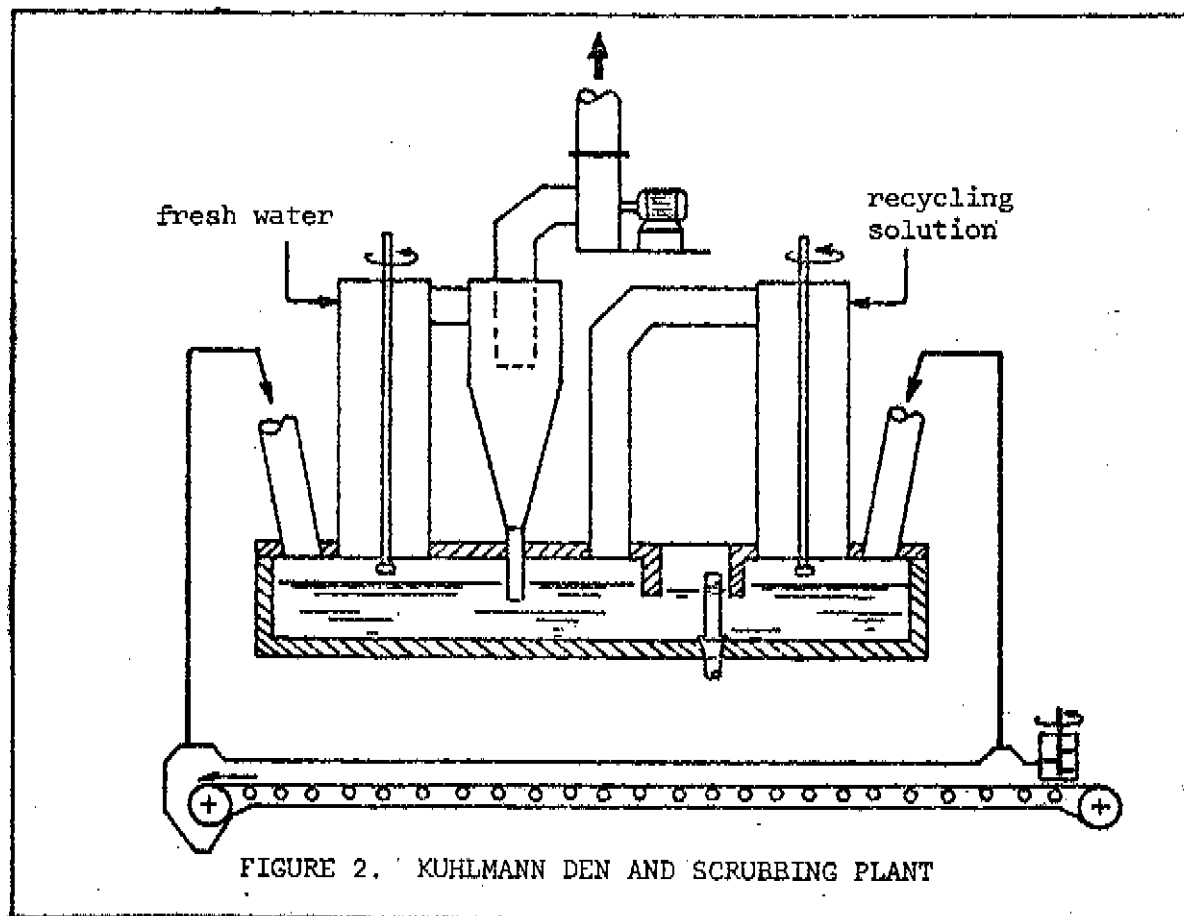
FIGURE 2. KUHLMANN DEN AND SCRUBBING PLANT
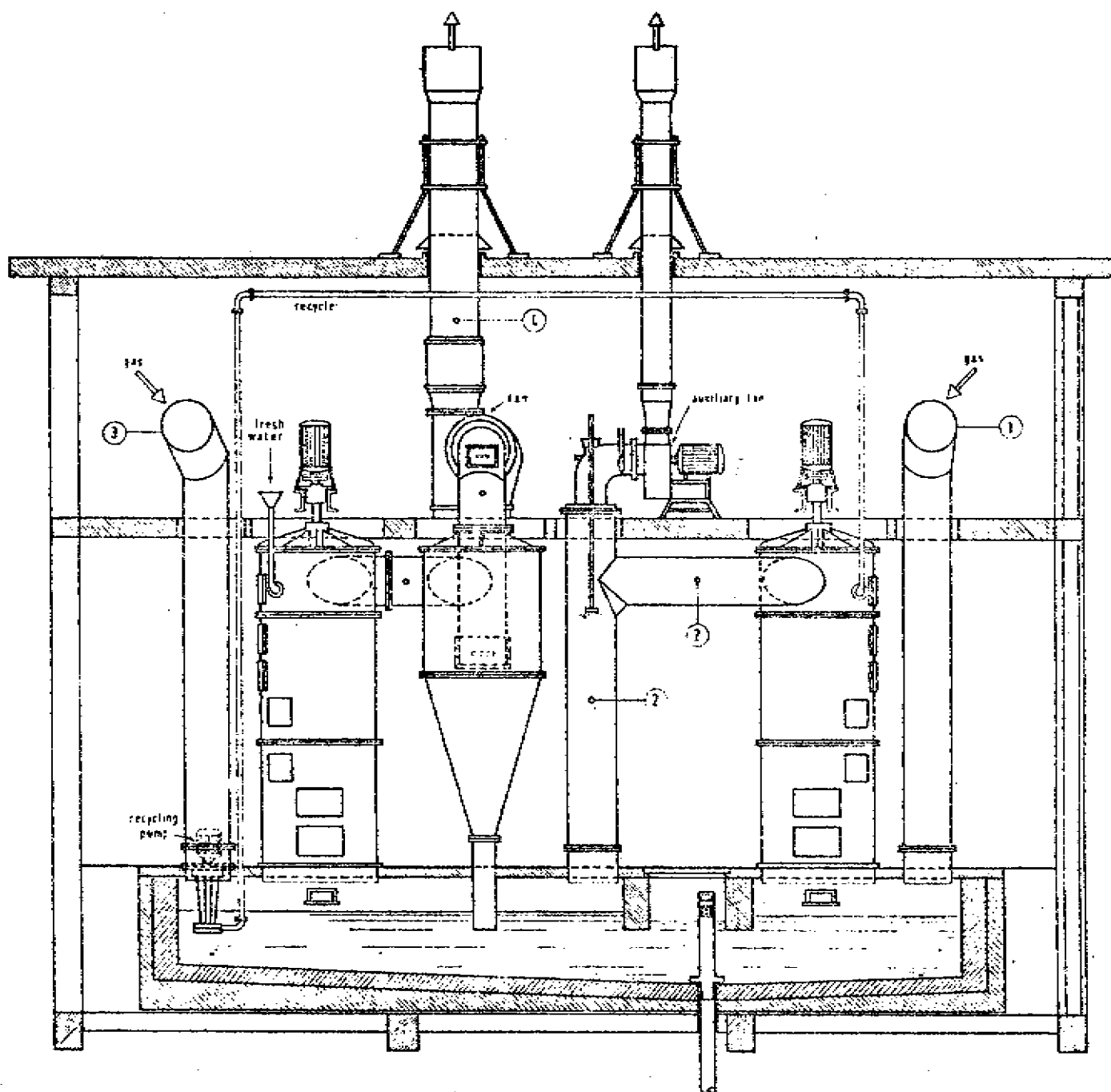
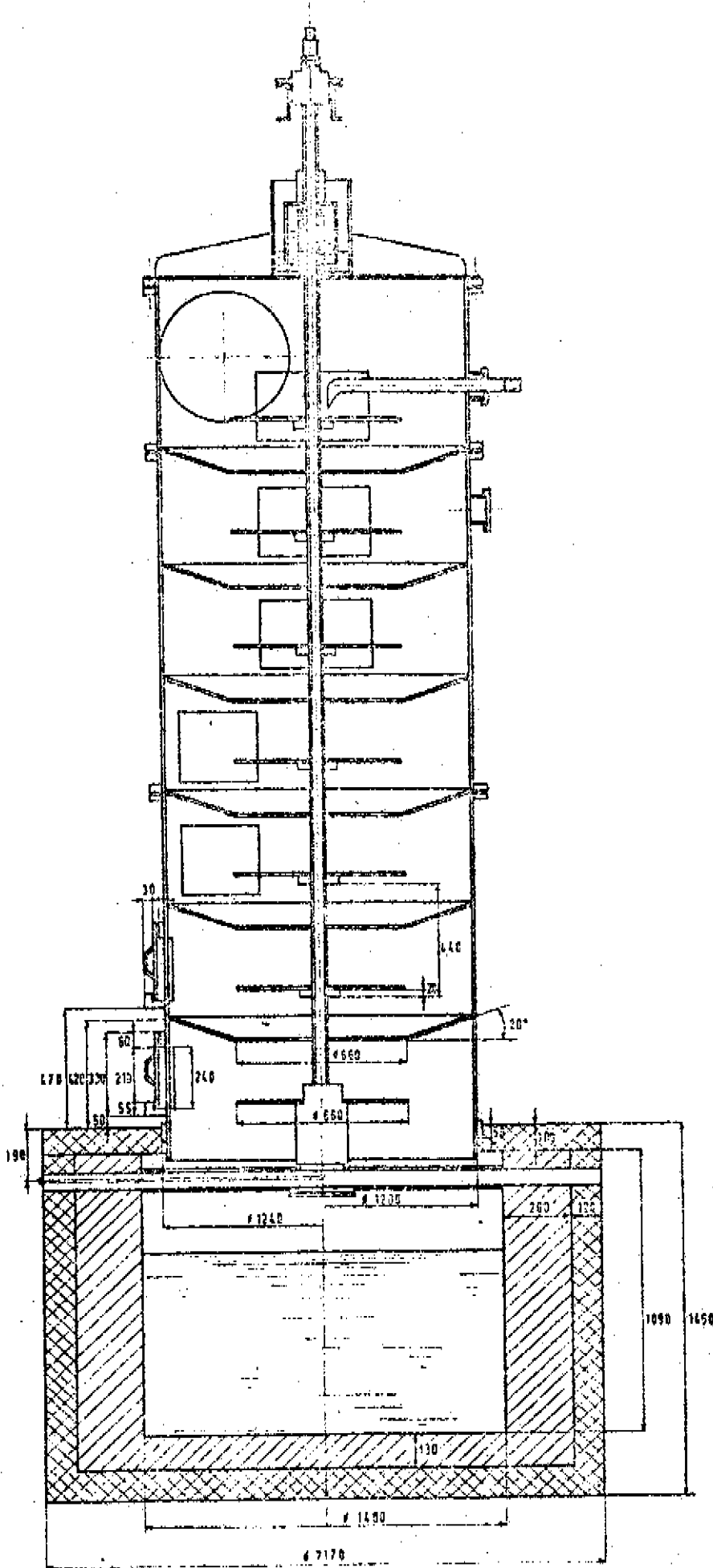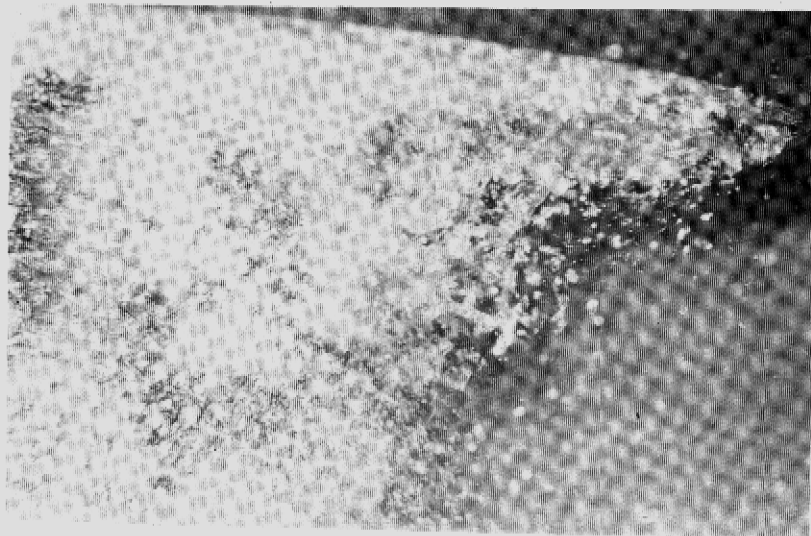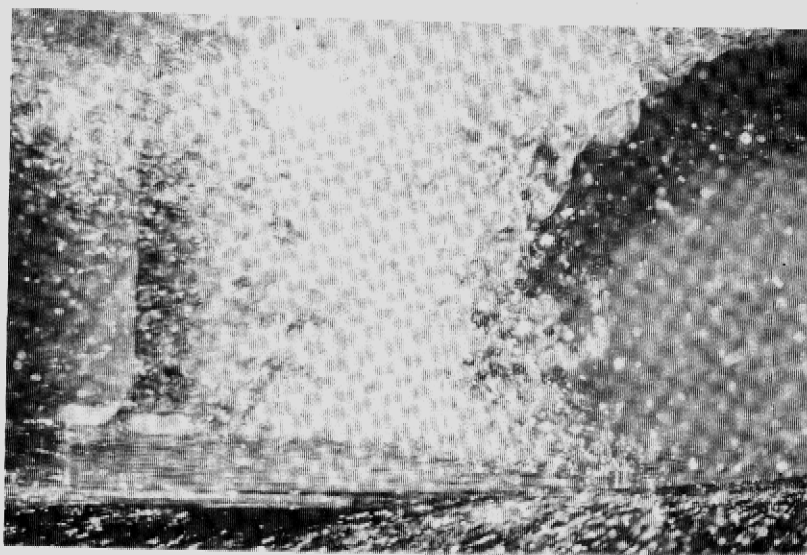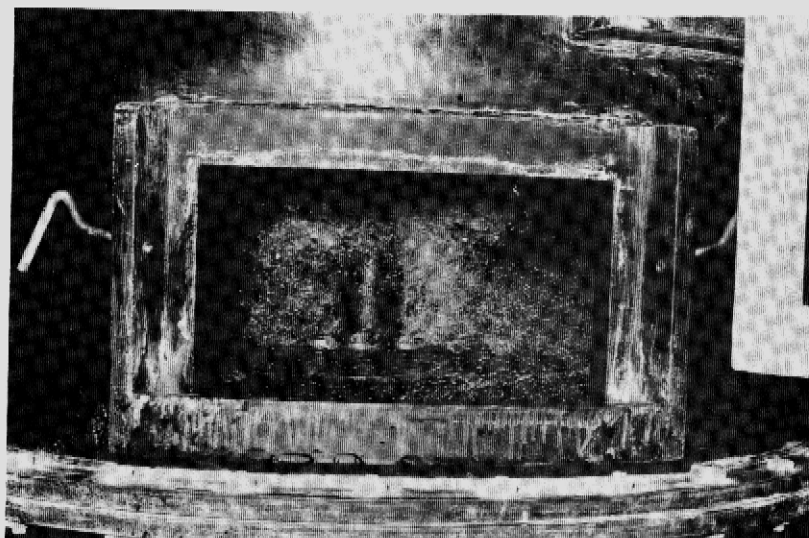Figure 3 -   PLAN OF SiF$_4$ SCRUBBING PLANT

FIGURE 4. ROTATING DISC TOWER

Fig. 5: Dispersion of drops: a) and b) first tower, L = 300 ℓ/min.;
c) second tower, L = 55 ℓ/min.