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SCRUBBERS FOR SUPERPHOSPHATE DEN GASES: AN APPROACH TO A RATIONAL DESIGN METHOD.

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INTRODUCTION

The need to operate and maintain gas scrubbing systems in connection with the manufacture of superphosphate in some 14 different factories has prompted the desire to study the performance in a number of cases with the object of acquiring data from which the design and construction of more effective and more satisfactory scrubbers can be achieved. Pressure from Government Departments concerned with atmospheric and river pollution has introduced more stringent requirements and the need in certain cases to neutralise or otherwise dispose of the effluent has also to be recognised. The cost of a scrubber suitable for the requirements in this country frequently is of the same order of magnitude as that of the den itself. This paper is an attempt to define the problem and to give certain facts and deductions arrived at over a number of years of study.

THE PROBLEM.

1.0 Acidulation.

During the acidulation of phosphate rock much heat is generated and gases are evolved which contain silicon tetrafluoride carbon dioxide, steam and even SO_2. Probably two-thirds of the fluorine which is liberated comes off during the initial slurry mixing and the remainder during the passage into and through the den.

1.1 Quantities Evolved from Continuous Den.

Measurements from discontinuous dens are complex, but the study of a continuous Broadfield den of conventional design making some 28 tons of superphosphate/hour has lead to an assessment of the quantities present as typified by the following table. In this case the mixer gases are evolved at approximately 78°C., and are diluted by air which passes into the den through various openings resulting in 6,000 c.f.m. of flue gases at a temperature of 600C.

TABLE 1.1 GASES EVOLVED FROM 28 ton DEN.

	Air	CO_2	SiF_4	H_2O	Total	H_2O Req'd to Saturate Gas
Mixer Gases @ 78°C.(x)						
lbs/hr. (16 tons/hour rock)	1470	1045	300	1250	4065	1250
lb. mols/hr.	50.7	23.7	2.9	69.5	146.8	-
Mols % of Total	34.5	16.1	2.0	47.4	-	-
Flue Gases @ 60°C.(+)						
lbs/hour	18,100	1045	490	2500	22,135	3000
lb mol/hr.	625	23.7	4.7	139	792.4	-
mols % of Total	78.9	3.0	0.6	17.5	-	-

(x) Would be saturated at 78°C.) Assuming CO_2 and SiF_4 behave
(+) " " " " 55°C.) as air in respect of saturation.

The volume of the mixer gases including air is, by comparison, 1,130 c.f.m. @ 78°C. In addition to the gases mentioned there may be SO_2 evolved and this presents an entirely separate problem which is touched on later in the paper.

1.21 Flourine Balance

The fluorine evolved corresponds to a loss from Morocco rock of approximately 1% of its weight and results in superphosphate having a fluorine content of approximately 1.7%. A typical fluorine balance over the den would be as follows:

	F - lbs/hr.
Entering mixer in rock	1,400
Leaving Den in Super	1,050
Leaving Den and Mixer in Gases	350

These figures represent the effect of using 64 units H_2SO_4 with 100 of rock phosphate, the acid strength being 70% w/w.

1.22 Water Balance.

A moisture balance leads to the following typical figures. The quantity of air drawn in from the atmosphere would carry with it 250 lbs/hour, which is small compared with the other quantities measured.

Entering Mixer in Acid	9,200	Leaving Den in superphosphate	7,150
" " " Rock	200	Leaving in Mixer Gases	1,250
" Den & Mixer in Air	250	Leaving in Den Gases	1,250
lbs/hour	9,650	lbs/hour	9,650

1.31 Fog Formation.

When air saturated with water vapour is mixed with air saturated at another temperature a fog is bound to result, (e.g. see psychrometric charts from "Air Conditioning Analysis" by Goodman, New York 1944). The gases leaving the mixture are almost certainly saturated, the evolution of steam setting a limit to the temperature rise of the mix. On admixture with cooler gases from other parts of the den, condensation in the flues will almost certainly result. As soon as these particles form, SiF_4 will be absorbed and react with the formation of fluosilicic acid and silica in accordance with the following or similar reaction:

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2 .$$

1.32 Condensation.

Dr. Whynes has shown that the vapour pressure of water in equilibrium with solutions of H_2SiF_6 falls off with increasing concentrations, so that as the diffusion of SiF_4 into the nucleii proceeds, there will tend to be a progressive growth in size of the mist nucleii by further condensation of water vapour. A sample of sludge taken from a ducting was found to have the following composition:

	Parts by weight
H_2SiF_6	25
SiO_2	5
H_2O	70
	100

This means that the concentration of H_2SiF_6 in the liquid phase is at least 26%.

The formation of silica flocs has also been noticed by Dr. Whynes in the laboratory; the flocs forming almost instantaneously with the contact of dry SiF_4 - containing gas with water vapour in a wetted wall column.

1.33 Moisture Sufficient Without Sprays

Earlier types of scrubber relied almost entirely on the self-precipitation of flocs of silica in a settling chamber in which some cooling was effected through the walls and time was afforded in which flocs could coalesce and reach a size at which they would readily settle to the bottom or on to trays. The moisture present in the gas stream is sufficient in itself to permit condensation of fluosilicic acid of a strength of not more than about 15% w/w if the gases be cooled to 0°C., and about 18% w/w when cooled to 30°C.

1.4 Two-fold Nature of the Problem.

The scrubbing problem resolves itself into two distinct parts;

(1) The absorption of SiF_4 vapour into a liquid phase which may be present in the form of mist or droplets, condensation on walls etc., or of liquid injected into the tower.

(2) The de-entrainment of mist particles consisting of aqueous solutions of fluosilicic acid and associated silica.

In many respects an apparatus suitable for one function would be suitable for the other, but the removal of very fine mists cannot be achieved so effectively without specially designed apparatus.(x) We do not know much about the size of the mist present but the two-fold problem must be recognised in the design.

1.5 Statutory Requirements in England.

In Great Britain the performance of a den scrubbing system is commonly judged by the Alkali Inspector on two counts, and generally speaking the tower may be considered satisfactory providing one or other condition is met: These are:

(a) that the exit gases leaving the scrubber should contain not more than 0.1 grains/cu. ft. of the SO_3 equivalent of H_2SiF_6. This corresponds in practice to .143 grains fluorine per cubic foot, or 0.33 gms F/M3. Assuming the F is present as SiF_4 the partial pressure represented amounts to 0.096 milliats.

(b) the efficiency of removal of fluorine as judged by the Fletcher's bellows tests applied to inlet and exit gas concentrations should be not less than 99%.

In practice these limits are minimum requirements and a better performance has in some cases been asked for.

(x) An account of the theory of impingement is given by Johnstone & Roberts, see Deposition of Aerosol particles from moving as streams. Ind. Eng. Chem. Nov. 1949, p.2417 et seq.

GAS ABSORPTION THEORY APPLIED TO DEN SCRUBBING.

2.0 Physical Characteristics of Existing Scrubbers Compared.

The principal characteristics of the scrubbing systems we have studied are shown in the summary sheet Table VI at the end of this paper, and this is discussed more fully under Section 3.4. The cost of a scrubber can be roughly related to its cubic capacity, although the cost of water and pumping may also be important, so that from a practical point of view the important criteria are:

(a) Volume of tower (cu.ft.) per ton of superphosphate per hour.
(b) Scrubbing liquid (gallons per minute) per ton of superphosphate per hour.

The range of such criteria are summarised thus:-

TABLE II - BASIC FACTORS COMPARED

	Batch Dens	Continuous Dens
	Spray Towers	
Column Ref. (Table VI)	8 - 10	1 - 7
Super tons/Hour	6 - 17.5	6 - 28
$\frac{\text{Tower cu.ft.}}{\text{Super tons/hour}}$ (a)	34 - 367	101 - 293
$\frac{\text{Liquid gals/min.}}{\text{Super tons/hour}}$ (b)	1.33 - 5.83	.75 - 6.07
	940 - 5930	1250 - 17000

The wide disparity in these figures indicates the lack of design data available for the economic design of satisfactory scrubbers, and arises from the empirical methods used in the past.

The effectiveness of tower space would be expected to depend directly on the quantity of spray present in each cubic feet. Multiplying tower volume by liquor rate (per square feet of cross sectional area) and dividing by the superphosphate production rate results in the figures in the lower line of the table.

These coefficients all show wide divergencies, and are clearly unsatisfactory from the designing point of view.

2.1 Need to Apply Gas Film Theory etc., to Correlate Performance.

Gas Absorbers - Gas absorbers relying on condensation have been referred to. The perfomance may be improved by injecting additional spray water or even recirculated acid into the chambers, or by installing grid packings which are wholly irrigated by liquor, which again may consist of recirculated fluosilicic acid. Both these types provide means for:

(i) presenting a considerable area of liquid surface to promote absorption of the soluble gas.
(ii) they both provide sufaces on which small mist particles may be attached by impingement.

Information which is now available on the behaviour of SiF_4 shows it to be amenable to the accepted laws of gas diffusion and absorption where the gas is highly soluble and as shown by Dr. Whynes in the case of a liquid film flowing over a wetted wall, the rate of absorption is controlled by the gas film resistance, and not (except in special cases) by the liquid film resistance.

The gas film coefficient will be improved by raising the relative velocity of gas and scrubbing liquid. In packed towers the relative velocity is determined mainly by the gas velocity through the tower, and cross sections must be designed so that maximum advantage may be taken of this. In spray towers this relative velocity may be initially high near the nozzle but will quickly diminish to the steady terminal value determined by the size of the droplets. This size depends on the spray pressure and type of nozzle. Assuming a uniform distribution of spray over the tower cross section, a given volume of liquor sprayed into the tower will result in very similar conditions obtaining in every part of the tower space, i.e. at each point a similar number of droplets of certain size and relative velocity will be passing every second. Increasing the number of sprays will tend to increase the surface area in proportion.

2.1 Need to Apply Gas Film Theory etc., to Correlate Performance (Contd.)

In any part of the tower (volume dV)., the rate at which the SiF_4 is transferred to the liquid will be expressed by the product of the surface area available(+) (adV) the driving force due to the difference in pressure of the SiF_4 in the gas compared with the back pressure exerted by the liquid (p-pe), and the coefficient of mass transfer (Kg), thus:-

$$Kga(p-pe)dV$$

It will be apparent from what follows that an average value of the product Kga may be determined experimentally for a given installation, and can be used to compare the degree of useful work being done per unit volume of tower space; or more simply the effectiveness with which the spray is being used to trap the fluorine content of the gas in each cubic foot of tower space.

2.11 Evidence that Gas Film Controls in Spray Towers.

A study of the gas liquid equilibria referred to by Dr. Whynes shows that for acid concentrations below 20% w/w, the pressure of SiF_4 vapour in equilibrium is extremely low, even when the operating temperatures are in the neighbourhood of 50 to 70°C. This explains why it is possible to absorb the gases effectively by recirculated liquid of considerable strength without adversely affecting the efficiency of the unit. It enables a simple theory to be built up as to the factors affecting tower performance and the derivation of coefficients which will be useful in the design of new or extension of existing scrubbers.

A simple mathematical relationship can be arrived at(ø) between the gas flow GS, tower volume V, and ratio of inlet to exit gas concentrations r, which can be used to determine K_ga, the coefficient of mass transfer per unit of tower volume, by which the merits of individual towers can be compared.

Thus: $\log r = K_ga\frac{V}{GS}$

2.2 Application of Simple Absorption Theory.

Before considering the estimated values of K_ga in particular cases, it will be of interest to apply the simple theory to illustrate how an alteration to the gas volume may be expected to affect the performance of typical scrubbing installations. Later we will give experimental evidence in support of these conclusions.

2.21 Spray Tower.

The value of the gas film coefficient and the type of spray used is assumed constant for this argument. This implies that K_ga is also constant.

Supposing an existing tower has an efficiency of 99% or a performance ratio r_1 of inlet to outlet concentration of 100, the inlet being say 10, and exit 0.1 units respectively.

Suppose that without altering the rate of superphosphate (and therefore fluorine) production, the volume of gases entering the tower be halved. The new ratio r_2 is given by:

(+) For precise definition see table of nomenclature.

(ø) See appendices I & II giving derivation and units employed.

2.21 Spray Tower (Contd.)

$$\frac{\log r_2}{\log r_1} = \frac{K_g aV}{K_g aV} \times \frac{G_1}{G_2} = \frac{G_1}{G_2} = 2$$

$$\log r_2 = 2 \log r_1$$

$$r_2 = r_1^2\text{, or an efficiency of } 99.99$$

The inlet concentration will have been doubled and the exit concentration becomes .002 units.

Alternatively, to preserve an exit of 0.1, the performance ratio of the new tower would need to be 200, requiring a new volume.

V_2, thus

$$\frac{\log r_2}{\log r_1} = \frac{K_g a\ V_2\ G_1}{K_g a\ V_1\ G_2} = \frac{V_2}{V_1}\ \frac{1}{0.5}$$

$$0.5 \times \frac{\log 200}{\log 100} = \frac{V_2}{V_1} = 0.5 \times \frac{2.301}{2.0} = .575$$

Thus halving the gas velocity would permit the use of a tower .575 of the original volume while preserving the original exit concentration. Alternatively it can be shown that a tower of half the original size would preserve the original efficiency, though the exit concentration would be doubled, i.e. 0.2

The importance of keeping the gas volume to a minimum is obvious.

2.22 Packed Towers.

A packed tower should be designed to have the maximum practical velocity of gas through the slats to obtain the most beneficial gas film coefficient, which will be expected to vary in proportion to $(G)^{0.8}$, (ref. Perry 2nd Edition, p. 1169, and the current paper by Dr. Whynes). This maximum velocity will be of the order of 5 - 6 ft/sec. for the packings employed, based on the empty cross section.

A reduction of gas flow to one half the design value will give a new performance derived as follows:

$$\frac{\log r_1}{\log r_2} = \left(\frac{G_1}{G_2}\right)^{0.8} \left(\frac{G_2}{G_1}\right) = \left(\frac{G_2}{G_1}\right)^{0.2}$$

$$\frac{\log(100)}{\log r_2} = (.5)^{0.2}$$

$$\frac{\log r_2}{10} = \frac{2}{(.5)^{.2}} = \frac{2}{.869} = 2.31$$

$$r_2 = 204 \text{ corresponding to an "efficiency" of } 99.5\%$$

Since the gas concentration Y, at inlet has been doubled, the exit Y_2 will now be $\frac{2 \times 10}{204} = .098$, i.e. there is practically no difference in this value.

Thus a reduction of gas flow to half has rather more than doubled the performance ratio, but the exit gas concentration is almost unchanged.

On the other hand a tower of exactly half the original volume would give an identical performance ratio providing the

2.22 Packed Towers (Contd.)

original gas velocity be retained by halving the cross section at each point. This deduction is comparable with that arrived at for spray towers.

Thus:

$$\frac{\log r_1}{\log r_2} = \frac{G_1^{0.8} V_1 S_2 G_2}{G_2^{0.8} V_2 S_1 G_1} = \frac{V_1 S_2}{V_2 S_1} = 1$$

This shows the importance of correctly estimating the minimum gas flow permissible, and designing the tower accordingly, the cross section of the tower being then in direct proportion to the gas volume to be passed through.

2.23 Jet Scrubbers.

This is a special case of a spray tower, in which a high pressure jet is hurled into the throat of a venturi shaped tube through which the gases pass. The jet exerts a pumping action and it follows that there must be considerable slip between the liquid droplets and the gas at the throat, and more especially near the nozzle itself where the gas velocity will be minimum and the jet velocity in the order of 90 f.p.s.

Halving the gas flow would result in a halving of the gas velocit at the throat and the subsequent tail section, and this would greatly increase the relative velocity between the liquid droplets and gas in this section. We have no way of checking what this slip would amount to in the two cases or in the various parts of the apparatus, but undoubtedly the transfer coefficient would be increased considerably at every point by reducing the gas velocity.

Halving the gas flow would double the residence time, which by analogy with the spray tower would result in a reduction in the exit concentration in the ratio 50:1, but the simultaneous increase in transfer coefficients would make the apparatus still more sensitive to such a change.

2.24 The above findings are conveniently summarised in the following Table:

TABLE III - EFFECT OF GAS FLOW ON SCRUBBER PERFORMANCE.

	Effect of halving gas flow in existing system	Size required to retain 0.1 exit	Size required to retain 99% efficiency
Spray Tower with typical standard performance. Inlet 10.0 exit 0.1, effy. 99	Effy.99.99 exit 0.1	.575 V exit 0.1	.5 V, exit 0.2
Packed Tower with typical standard performance. Inlet 10.0, exit 0.1, effy. .99	Effy. 99.5, exit .098	do providing cross section is halved to maintain original gas velocity.	do
Jet Type with typical standard performance Inlet 10.0, exit 0.1, effy. 99	Over 99.99%	Comparison expected to be rather more favourable than packed tower owing to improved coefficient of mass transfer at higher relative liquid/gas velocities.	

SPECIAL INVESTIGATIONS ON EXISTING SCRUBBERS.

3.0 Types Investigated.

It may now be of interest to deal briefly with some of the installations we have studied in more or less detail, and illustrate their performance in relation to the theories already advanced.

The types studied are:

(1) Spray tower with low performance coefficient, K_ga.
(2) Packed tower system with higher coefficient.
(3) Jet type two stage scrubber, with highest coefficient.

3.1 Spray Tower at Cliff Quay.

This consists essentially of six square brick towers built in a block, each section measuring internally 7 ft. square and 28 ft. high above the liquor level. The gas enters the top of No. 1 section, passing alternatively up and down, and leaves at the top of No. 6 section, to which the fan is connected. In the first place water was fed through 24 sprays each taking 8 lbs. water per minute at a pressure of 8 p.s.i.

The gases from the mixer and Broadfield den itself combine and are drawn along a flue some 30 ft. long. This is a brick lined cast iron and has wooden cover boards. The gases entering the tower have a composition (with Morocco rock) typified in section 1.1.

Experiments made on this system in which the flourine absorption in successive sections, and in the first section when acid liquor was recirculated, will now be described.

The liguor holding capacity of the sumps in the tower bases amounts to about 75 cu. ft. so that difficulty was sometimes encountered in establishing steady running conditions; but in some of the later experiments the base was shaped in such a way as to reduce this hold up to a few gallons.

3.12 Fluorine Evolution Dependent on Ambient Temperature.

Although not at first suspected, examination of a considerable number of records shows that the fluorine evolution varies in sympathy with the ambient temperature. A plot of these records is shown in Fig. 1.

It is not yet established that the extrapolation suggested by the curves is valid, but a distribution over twelve months as shown in Fig 2 may reasonably be expected.

3.13 "r" Values in Successive Tower Passes.

The absorption of F in each of the successive sections of the tower is illustrated by the following table in the case where similar quantities of water are sprayed into each section. The F quantities are calculated on the assumption of equal volumes of liquor leaving each section of the tower, from their F contents, and from the measured quantity of F in the exit gas stream.

A rather higher performance ratio is noticeable in the sixth section, but this is explained by the fact that some packing is included in this section and this is known to be effective in removing silica flocs from the gas stream. When the values of the mass transfer coefficient per unit volume are calculated, it is seen that they are quite consistent apart from No. 6 section.

3.13 "r" Values in Successive Tower Passes (Contd.)

TABLE IV. - "r" VALUES IN SUCCESSIVE TOWER PASSES.

Section No.	%F pick-up	F Flow % of inlet	$\frac{Y_1}{Y_2}$ for each stage	$\log_e \frac{Y_1}{Y_2}$	$K_g a$
1	30	100 70	1.428	.357	.305
2	25	45	1.555	.442	.378
3	16	29	1.552	.439	.376
4	13	16	1.812	.594	.508
5	7	9	1.779	.575	.491
6	8	1	9.00	2.19	1.87
To Stack	1				

Dr Whynes reports that absorption of SiF_4 in water droplets failed to rise proportionately when the concentration of SiF_4 in the gas phase increased above 80 mm. Hg or 105 milliats. The concentration in the first tower section was about 3 grains/cu. ft. (Alkali Inspectors' units) or 0.096(3.0/0.1) = 2.88 milliats, so that we should not expect to encounter this phenomenon in the present case.

3.14 Effect of Varying Sprays in 1st Section of Tower.

In another series of experiments on the strong gas section of this tower the number type and disposition of sprays was varied to include a rather wide range of commercially practicable arrangements. Water was fed to the sprays in measured quantities, while the acid concentration of the liquor leaving this and all the other sections was measured as in earlier experiments. The percentage pick up in No. 1 section was then calculated, and shown as a function of liquor rate in Fig. 3. This shows that the F pick-up is controlled largely by the quantity of water fed to the tower, and much less by the type or number of sprays used. There is thus little advantage to be gained in using a multiplicity of small sprays where one large one will do, especially where this permits larger portways and less likelihood of blockage. The three types of spray used in these experiments are shown in Fig 4, and these give cones of spray within the following limits:

A	60 to 90°	with pressure	8 to 15 p.s.i.	Solid cone.
B	28 " 35	" "	9 to 26 p.s.i.	Hollow cone.
C	35 " 40	" "	9 to 26 p.s.i.	Hollow cone.

3.15 Effect of Increasing Acid Strength.

In a further test the acid made in sections 1 and 2 taken together were recirculated to a spray at the top of No. 1 section. Acid was removed steadily from the system and make up water added at the top of No. 2 section to keep the strength at the desired value. For a number of different acid concentrations the F pick-up was measured and the results are plotted in Fig. 5. This shows a steady absorption rate up to 15%, followed by a rapid fall-off as concentrations of 25% are approached. This is to be expected since the vapour pressure exerted by acid of 20% w/w and upwards increases rapidly, and the concentrations at the surface of the drops may well be higher than the <u>average</u>, corresponding to the development of a liquid film resistance.

3.2 Packed Scrubbers at Bo'ness.

These scrubbers were designed for a gas flow of 6,000 c.f.m. in a series of rubber lined steel towers having a cross sectional area measuring 4' x 4'. Alternatively they can be divided to form double pass units 4' x 2' suitable for 3,000 c.f.m.

Owing to difficulties experienced with blockage of the packing in the first tower in the series, the packings were removed and replaced by sprays. The data reported refers to the performance of the second and third passes in which the original packing has been successfully operated for nearly two years.

Each pass has an independent circulating pump feeding the packing through trough distributors. The towers serve at 6 t.p.h. continuous superphosphate den, the gas flow being 3,000 c.f.m. The packing consists of rectangular wooden grids resting one on another and arranged as follows, the cross section in use being 4 ft. x 2 ft. in both cases.

<u>TABLE V</u> - <u>PACKING DETAILS AT BO'NESS</u>.

	2nd pass (up flow)		3rd pass (down flow)	
	Height	Type	Height	Type
Upper	12"	¾"x3"x4"spacing	12"	¾"x3"x4"spacing
			12"	½"x2"x1¾" ..
Intermediate	13'-6"	½"x2"x1¼ ..	12'-6"	⅜"x2"x1" ..
Lower	12"	¾"x3"x4" ..	12"	¾"x3"x4" ..
Circulating Liquor:	4.8% H_2SiF6		1.0%	
Temp. do	33°C.		28°C.	

Appropriate overall coefficients for the two sections of the tower are calculated in Table VI, and amount to 3.68 mols/hr.ft^{3}atm. which is three or four times greater than for the Cliff Quay spray tower; this figure being based on the gross volume of the tower and not just the packed space itself.

3.3 Jet Scrubbers.

The principle of the jet condensers has been referred to in paragraph 2.23. Our experience relates to a recent installation serving a Moritz den working up to 28 t.p.h. superphosphate.

The plant consists of two almost identical units in series, with circulating liquor in the second stage being fed as make up to the first, from which acid of up to 10% H_2SiF_6 is bled. Each unit comprises a vertical venturi shaped pipe approximately 13' high standing on a horizontal cylindrical tank 8' in dia., with simple baffles to reduce carry over of spray. Vertical spindle glandless Stokes pumps circulate acid liquor at a rate of 300 g.p.m. and pressure of 45 p.s.i. to a specially shaped nozzle. The cone of spray diverges sufficiently to fill the 16" dia. throat of the venturi. Inter-connecting ductwork is 24" dia. throughout.

The system was intended to handle 6,000 c.f.m. but in practice about 3,000 c.f.m. is usual.

3.31 Temperature Limitations.

Early experience gave a disappointing performance ratio and the gas volume was reduced to the minimum practical value sufficient to prevent escape of gases from the den. The performance improved (as may be expected) but we were concerned at the high operating temperature in the first unit and feed ductwork, which ran as 70 to 74°C. This was considered too hot for safety of the rubber lining, and a compromise was adopted. This consisted in:

(a) raising the gas flow to 3,000 c.f.m.
(b) passing the gases through a length of old concrete flue to promote some cooling.

The resulting operating temperature was thus reduced to slightly below 70°C.

3.32 Improvement in Performance.

Improvement in performance ratio was gained by standing the primary condenser on a nine foot length of duct which acted as additional spray tower using the liquid falling from the venturi pipe. This had the effect of reducing the exit gas value from .25 to .15 AA(x) units. It was not practicable to follow suit with the secondary.

3.33 Complication of SO_2.

Unfortunately our investigations are as yet incomplete, but it would appear that the performance ratio on F is in fact very high. More recently it has been discovered that SO_2 is present in the gases in appreciable amount and attention has been turned to the source of this contaminant. The superphosphate is made from contact acid known to contain SO_2 in quantity equivalent to the proportions found in the exit gases. Gafsa rock apparently liberated less SO_2 than Morocco, and this was confirmed by laboratory tests. A quantity of SO_2 free acid was then used in the plant, but contrary to expectation, SO_2 free acid was again found in the exit gases, though to a less extent than before. The SO_2 would therefore appear in part at any rate to depend on the reaction of phosphate rock and sulphuric acid, as well as partly to SO_2 present in the acid itself.

3.34 Calculation of Coefficient.

A value of 15.6 for K_ga is calculated in Table VI on conservative values for exit gas concentration, and the volume of "tower" assumed in the calculations is that of a cylinder embracing the whole of the venturi pipe from the top or jet level down to the level of the liquid in the tank below.

The figure does however bring out the high K_ga of the jet condenser and its immediate ductwork as compared with spray towers, or packed towers, though the relative volume of plant including separating tanks would be rather less favourable than this criterion alone would indicate. Nevertheless, the capital cost of an equivalent tower system would be higher. The pumping costs tend to offset any such saving, but where installation room is limited or the den is operated intermittently this type of installation has a definite advantage in operating costs, subject, of course, to a satisfactory resolution of the problems of temperature and SO_2. Removal of the latter is not likely to be an easy problem in view of its very low solubility and the high recirculating temperature, and would seem to merit a review of the statutory limit to take account of this.

(x) "Alkali Act units", i.e. grains/cu. ft. SO_3 equivalent of H_2SiF_6. See 1.5(a).

3.4

Having dealt in some detail with the investigations on these three different types of installation, we may now consider what further evidence there is in support of the evaluation of performance in terms of the elementary concepts of absorption developed in 2.11.

The principal dimensions of some thirteen installations in our organisation, and their accepted operating characteristics have been brought together in Table VI, together with remarks listed on an adjacent page.

For convenience the range of some of the principal features of the first ten towers, all of which are more or less conventional spray towers, but differing widely in size and shape, is given in Table VII below:

TABLE VII - RANGE OF FACTORS INVOLVED IN SPRAY TOWERS - (Nos. 1 to 10 in Table VI).

	Min.	Max.	Ratio Max: Min:
Size of den - super, t.p.h.	6	28	4.7
Tower volume ft^3	590	8200	14
Gas flows c.f.m./super, t.p.h.	89	584	6.6
Gas Velocity f.p.s.	.73	7.6	10.4
Tower Volume ft^3/super, t.p.h.	101	367	3.6
Liquor flows g.p.m./tons super, p.h.	.75	6.07	8.1
Residence time	16	75	4.7
K_ga	.616	2.65	4.3
K_gA/L	.013	.258	20

The ratio of K_ga values is 4.3:1, which considering the range of individual factors involved, is perhaps surprisingly small. If however the special case of No. 10 is omitted, this being a batch den with long connecting flues, the range of K_ga is .616 to 1.71, or 2.8:1 which is more satisfactory.

The range for K_ga/L is however disappointingly large at 20:1. The explanation seems to be that in those cases where high liquor rates are used, the droplet sizes are much coarser, and the method of spraying is relatively ineffective because a great deal hits the adjacent walls of the tower.

Some comments on the individual cases arranged in order of magnitude of K_ga are given in Table VIII. The packed tower and jet scrubber take their expected places in this table, with K_ga of 3.7 and 15.6 respectively, but the low K_ga/L, .0039, for the jets again shows the relative ineffectiveness, drop for drop, of the circulated liquid.

3.4 (Contd:)

TABLE VIII - TOWERS ARRANGED IN ORDER OF K_ga.

Ref:	Site	K_ga	K_ga/L	Remarks
11	NT	.49	.16	Batch den; unit consists of a large circular chamber and tangential inlets; probably short circuiting takes place.
1	CQ	.616	.259	This has been described in some detail in the text.
9	BG new	.638	.071	The low K_ga/L is not explained by the fact that this is a recirculating tower. The performance has not been studied much because of the difficulties of intermittent mixing (rock and acid).
2	AH	.710	.0129	The coefficients have been derived on the arbitrary assumption that the gas volume increased uniformly throughout its passage through the tower. The large quantities of wash water are not used so efficiently as in example 1.
3	AH Mor	.769	.0340	
8	BG Old	.938	.222	
6	SN	1.00	.0374	Vertical cylindrical wooden stave towers with copious water supply. Probably much of the water hits the sides, hence a low K_ga/L.
7	WS.	1.02	.0734	Information rather sketchy.
4	BLA	1.04	.128	This result is considered fairly reliable.
5	SH	1.71	.0802	Information is rather sketchy.
10	BK	2.65	.119	This high coefficient is partly due to the use of some packing, the great relative length of connecting flues and intermittent working. Water is distributed from holes in a flooded top cover.
12	BS	3.7	.06	Packed tower gives high K_ga. These figures relate to the second and third passes of a three tower system.
13	AH Jet	15.6	.004	Jet system gives maximum value of K_ga, but the large volume of liquid is evidently not so effectively used drop for drop as in spray systems.

4.0 PRACTICAL CONSIDERATIONS.

In the foregoing a number of practical aspects of operation have been taken for granted, and it may be of value to recount some of our experiences.

Development has been governed to some extent by materials of construction available. The earlier tower designer had no inhibitions and designed in brick using cement or even lime mortar joints. Fine water sprays of low consumption were employed. The lime formed a conveniently hard reaction product with H_2SiF_6 and many such towers lasted over half a century or more, although they would not be regarded as good neighbours at such an age.

The peak rate of mixing in the older batch dens is high, the area of openings small, and relatively low gas volumes are involved. Correspondingly high inlet gas concentrations and "r" values are found.

4.0 Practical Considerations.(Contd.)

The towers were thus comparatively large and the dens working intermittenly allowed ample time for cooling between use and facilitated condensation. There was plenty of time for cleaning flues etc., and labour was cheap.

Our present view and experience is that the most satisfactory type of massive construction is in good quality engineering brick, without frogs, bonded with a latex hydraulic type of cement. Except for organic resin based cements, which are expensive, most other types (particularly silicate) are susceptible to erosion, and are therefore unsatisfactory with high liquor rates.

Many of the older effluent systems employed asseries of catch pits which collected silica deposits which were religiously cleaned at frequent intervals. It has been found perfectly practical to dispose of effluents by pumping to considerable distances in polythene or rubber lined piping, a possibility that permits with the same pump of recirculation over the scrubber and improved performance. Similarly the attention required to cleaning of towers can greatly be reduced by using adequate spray liquor and reducing to the minimum all idle volumes of liquor where sedimentation can take place. The silica must be kept on the move. All these points are of increasing importance with modern continuous dens where idle time costs money.

The use of rubber lined steel for ductwork, washtowers, or jet condensers has been found satisfactory although our experience does not cover more than a few years. The temperature limitation has already been mentioned. Nevertheless, this form of construction leads to clean, leak free plants and being much lighter than corresponding flues enables more compact and satisfactory layouts, which may be placed very close to the den itself. A further feature of occasional importance is the possibility of re-siting in a case where future development of an old factory is expected to involve repositioning of the superphosphate den.

For pipe lines polythene and rubber lined steel are equally satisfactory. More recently the adoption of reinforced rubber hose with integral flanges has been favoured, and this is especially attractive owing to the slight flexibility which deters the build-up of silica deposits on the walls. Normally this is not a serious feature, but where high temperatures are experienced the silica crust can be extremely hard and we have as yet found no satisfactory method of overcoming it.

Timber packings have given satisfactory service over periods of two years, but their use must be confined to cases where thorough irrigation can be assured. If for example, the easiest way to clean out adjoining ductwork is to rake the silica deposits forward into the upper part of the tower, partial blockage is bound to result in time. The gradual encrustation of the timber by silica nevertheless does proceed and when this becomes excessive the efficient wetting of the surfaces by the circulating liquor will be impaired and the trouble will develop apace. Similar remarks apply to spray towers in which the walls are insufficiently irrigated. This allows thick irregular deposits to accumulate and develop runnels in which much of the spray is conducted to the floor without doing useful work.

Wherever liquor has to be recirculated the type of metal to be used for pumps, spray manifolds and etc., has to be considered. Our experience has shown that monel metal and high chromium-molybdenum-nickel alloys, such as Langalloy 5R and LaBour R55, are the best suited for this duty. American reports suggest that more common materials such as brass and copper are satisfactory, but we have made no real use of them. Lead is not satisfactory, with strong acid as it is susceptible to erosion, particularly when silica is carried in suspension.

Although pumps with horizontal packed spindles are used, for example the LaBour type, we prefer wherever possible to design the tower sumps for use with glandless vertical spindle pumps which give practically no trouble in operation. They must be placed so that liquor gravitates to the entrance to the impeller.

Some typical sprays are described in section 3.14. Monel metal has been used for the smaller sizes but ebonite is equally resistant though more easily damaged. One good spray with a big hole gives far less trouble than a lot of smaller ones. There is no virtue in some of the fancy internal work seen in some designs. Two large tangential approaches to the swirl section are probably ideal.

Sprays should never be inserted at the side of a tower. They seldom remain in position and they have less height in which to operate. The spread of the jet is important, as it must not hit the sides too high up. The geometry of the tower passes is important in the same connection: a relatively high tower will tend to give more uniform flow of gas and will be less liable to "channelling", i.e. short-circuiting of the gas with consequent inefficiency.

4.1 The Design Problem.

Sufficient has been said of the performance of existing scrubbers, and we conclude our paper by summing up the principles required in designing a satisfactory installation.

It is of prime importance to reduce the volume of gases to the minimum compatible with (a), operation of the den without escape, (b) the reduction of gas temperature. The latter is likely to be the limiting factor if rubber lined steel is to be used, or with recirculating systems, and for 28 tons super per hour means 4 to 5,000 c.f.m. For brick towers and straight through washing, a volume of 3,000 c.f.m. should be adequate providing the den is of the Moritz type, or is a Broadfield den with fixed (not slatted) sides.

If disposal of effluent by pumping is attractive, there should be no hesitation in adopting recirculation, especially where water costs are high. The height of the tower may be decided by reference to local buildings, height of the den etc., and we suggest the cross-section should be approximately 1/6 of this and not less than 4 ft., except in the case of packings which should be designed on a basis of 5 to 6 f.p.s. on the empty tower. Application of the formula (para. 2.11) will suggest the volume necessary for any desired performance, choosing a $K_g a$ value from the Table of data (Table VI). This will decide the number of passes necessary and the exact number (odd or even) will depend on the layout in relation to the stack. We prefer to have the fan at the exit from the tower to avoid build up, and there is usually no difficulty in arranging this above the tower so reducing the height of discharge duct-work required.

ACKNOWLEDGMENT

Acknowledgment is made to the Directors of Fisons Limited for permission to present this paper, and to colleagues who have carried out experimental work and assisted in tabulating the considerable amount of data represented by the Tables.

APPENDIX I.

Symbols Used	
a	Interfacial area, ft^2/ft^3 tower space.
G	Molar mass velocity of gas, lb.moles/hr.ft^2 of tower cross section.
G'	Superficial mass velocity of inert gas, lb.moles/hr.ft^2 of tower cross section.
G_1	Molar mass velocity of gas at inlet, lb.moles/hr.ft^2 (x)
G_2	Molar mass velocity of gas at exit, lb.moles/hr.ft^2 (x)
Gm	Log mean molar mass velocity of gas $(G_2-G_1)/\ln G_2/G_1$ lb moles/hr.ft^2
K_g	Gas film coefficient, lb.moles/hr.ft^2 atm.
l	Total effective height of absorption system, ft.
L	Liquor rate, lb.moles/hr.ft^2 cross-sectional area.
L'	Liguor rate, lb.moles solvent/hr.ft^2 cross-sectional area.
p	Partial pressure of solute in main gas stream, atm.
pe	Pressure of solute in equilibrium with main body of liquid, atm.
r	Ratio of inlet: exit mole fractions, y_1/y_2
S	Flow cross-sectional area ft^2
V	Volume of absorption system, ft^3
y	Mole fraction of solute in gas stream.
y_e	Mole fraction of solute in gas stream at equilibrium with bulk of liquid.
y_1	Mole fraction of solute in gas stream at inlet.
y_2	Mole fraction of solute in gas stream at exit.
Y_1	Concentration of solute in gas stream at inlet, grains equivalent SO_3/ft^3.
Y_2	Concentration of solute in gas stream at exit, grains equivalent SO_3/ft^3.

(x) Except in 2.21 and 2.22 where the meanings of G_1 and G_2 are apparent from the text.

APPENDIX II.

DERIVATION OF COEFFICIENT OF MASS TRANSFER.

The general equation for absorption in the case where the gas film is controlling may be written:-

$$\overset{\text{total mols gas/hr.ft}^2}{G}.\overset{\text{change in mole ft. solute gas}}{dy} = \overset{\text{gas film coefficient, lb.moles/hr.ft}^2\text{ atm.}}{K_g}\ \overset{\text{partial pressure difference from gas to bulk of liquid, atm.}}{(y-ye)}\ \overset{\text{effective surface area in volume of tower concerned.}}{adh}$$

this assumes:-

(1) the mean partial pressure of the inert carrier gas is essentially constant and equal to the total pressure (1 atm.)

(2) K_ga remains constant through the system.

(3) The gas is dilute i.e. $G = G^1$

from the above equation,

$${}_{y_2}^{y^1}\ \frac{dy}{y - ye} = {}_{o}^{1}\ \frac{K_ga.dh}{G}$$

For the case where ye is negligible, the expression simplified to:-

$$\ln \frac{y_1}{y_2} = \frac{K_ga\ l}{G} = \frac{K_ga\ V}{GS}$$

$$\therefore \quad \ln r = K_ga \times \frac{\text{system volume}}{\text{total gas flow}} \qquad 1.$$

Similarly, for the case where leakage of air into the system leads to a steady increase in gas flow from G_1 to G_2 from entrance to exit:-

$$\frac{dy}{y} + \frac{dG}{G} = \frac{K_ga.dl}{G}$$

From this, $\ln \frac{y_1}{y_2} + \ln \frac{G_1}{G_2} = \ln \frac{y_1G_1}{y_2G_2} = \frac{K_ga\ V}{Gm\ S}$ 2.

where $Gm = \dfrac{G_2 - G_1}{\ln \dfrac{G_2}{G_1}}$

TABLE VI - PRINCIPAL FEATURES AND DERIVATIONS FOR THIRTEEN TOWERS IN FISONS WORKS.

(See notes on adjacent pages and descriptions in section 3.4).

1 Column Reference		1	2	3	4	5	6	7	8	9	10	11	12	13
2 Site		Cliff Quay	Avonmouth	Avonmouth	Blaydon	Silloth	Silvertown	Widnes	Barking	Barking	Berwick	Newport	Bo' Ness	Avonmouth
3 Plant		Broadfield	Broadfield	Moritz	Maxwell	Maxwell	Broadfield	Broadfield	Moritz	Moritz	Sturtevant	Svenska	Broadfield	Moritz
4 Type		Continuous-Spray Towers							Batch - Spray Towers				Continuous Packed Tower	Continuous Jet System
5 Super output	ton/hr..	28	28	25	9	6	12.5	9	6	6	17.5	20	6.5	25
6 Flourine in gas Y_1	grains SO_3/ ft^3 @ n.t.p.	3.0	6.41	9.93	5.66	1.5	4.5	3.27	13.1	11.2	14.09	31.7	1.74	9.2
7 Flourine in exit gas Y2	do	.04	.05	.066	.052	.033	.09	.029	.13	.09	.23	.59	.12	.21
8 Efficiency $\frac{(Y_1xY2) \times 100}{Y_1}$		98.6	99.2	99.3	99.0	97.8	98.0	99.1	99.0	99.2	98.5	98.2	93.1	97.8
9 Gas rate as reported	ft^3/min.	7000	2500 -13000 (log mean 6380)	3750 -18400 (log mean 9200)	1200	3500	3150	3400	1500	1750	2280	2500	3000	3000
Inlet gas rate est'd from super rate and gas analysis		10,000	4700	2710	1710	4300	2980	2950	490	575	1330	680	4000	2920
10 Tower Volume V	ft^3	8200	4800	6850	910	1300	2050	2640	1230	2200	590	3380	363	121
11 Tower Pass Cross-Section	ft^2	49	14.7	36	26.1	9	12.5	15.4	9	10-40 (av.26)	5.0	183	8	2.49
12 Effective height x no. of passes	ft.	28 x 6	47 x 7	38 x 5	17.5x2	36x4	32.5x4 17x2	24.5x7	20x7	17x5	13x9	18.5x1	22.5x2	28.8x1 19.8x1
13 Gas Velocity in Tower	ft/sec	2.4	2.8-14.7	1.7-8.5	.77	6.5	4.2	3.7	2.8	.73-2.9	7.6	.23	6.3	-
14 Total number of sprays		24	28	20	4	23	12	18	15	10	Holes	21	-	-

	Column Reference		1	2	3	4	5	6	7	8	9	10	11	12	13
15	Total water usage	g.p.m.	2	170	122	12.8	23	60	45	8	15	30	17	-	10
16	Circultating rate (if used)	g.p.m.	21	-	-	-	-	-	-	-	35	-	-	30	300
17	Water Source		Town	Sea & Rhine	Sea & Rhine	Town	Town	Thames River	Town	Town	Town	Bore-Hole	Town	Town	Town
18	Gas rate/super rate	ft^3/min/ton/hr.	250	89-464	150-736	133	584	252	378	250	292	130	125	462	120
19	Tower Volume/ super rate	ft^3/ton/hr.	293	171	274	101	217	164	293	205	367	34	-	-	4.8
20	Scrubbing rate/ super rate	g.p.m./ton/hr.	.75	6.07	4.9	1.42	3.84	4.8	5.0	1.33	5.83	1.72	-	-	12.0
21	Hold-up time for gas	sec.	70	37	37	46	22	39	47	49	75	16	81	7.3	2.4
22	Ratio of F concentrations	Y_1/Y_2	75	128	150	109	45.5	50	113	100	124	61.2	53.7	14.5	43.8
23	$l_n Y1/Y_2$ ($+l_n G_1/G_2$)		4.32	3.20	3.42	4.69	3.81	3.91	4.72	4.60	4.81	4.11	3.98	2.67	3.78
24	Gas rate, GS	mol.air/hr.	1170	1065	1540	201	585	526	568	251	292	381	417	501	501
25	Liquor rate/area, L	mols.water/hr.ft^2	2.38	55.0	22.6	8.15	21.3	26.7	13.9	4.23	8.97	22.2	3.1	62.5	4020
26	$K_g a$	mol/hr.ft^3.atm.	0.616	.710	.769	1.04	1.71	1.00	1.02	.938	.638	2.65	.492	3.68	15.6
27	$K_g a/L$		.259	.0129	.0340	.128	.0802	.0374	.0734	.222	.0712	.119	.159	.0589	.00389
	Reference No. (see Notes)		1,10	2	2	10		5		3,11	4,10,11	6,7	6,7	7,8	9

NOTES ON COMPILATION OF TABLE VI.

Ref: No. — Remarks

1. In this case the fact that a strong acid liquor is produced explains the low water usage.

2. For both these cases (columns 2 and 3) the air flows through the systems increased considerably as indicated due to air leakage. For calculation purposes, the log mean value of the flow was used and the fluorine concentrations are corrected,

   (i.e. loge $\frac{G_1}{G_2}$ is added to loge $\frac{y_1}{y_2}$)

3. This system has now been replaced by that shown in column 9.

4. In this system the passes vary in cross-sectional area and an average value has been used for calculation purposes.

5. This installation no longer operates.

6. The figures in these columns (10 and 11) are based on an average rate for the mixing cycle.

7. The data here refers to part of the installed system only.

8. The figure for K_ga/L has no theoretical justification in the case of a packed tower but is given for comparison only. The gross tower volume is used for calculation.

9. These figures are calculated on the effective scrubbing portion of the system for comparison purposes.

10. These installations though predominantly spray systems, include some packed sections.

11. These two systems, although having continuous dens, have batch mixers and hence inlet gas compositions are liable to wide fluctuations.

N.B. For this table, the ratio $\frac{Y_1}{Y_2}$ is assumed equal to $\frac{y_1}{y_2}$ and both gas and liquor are assumed dilute,

(i.e. $G = G^1$ and $L = L^1$).

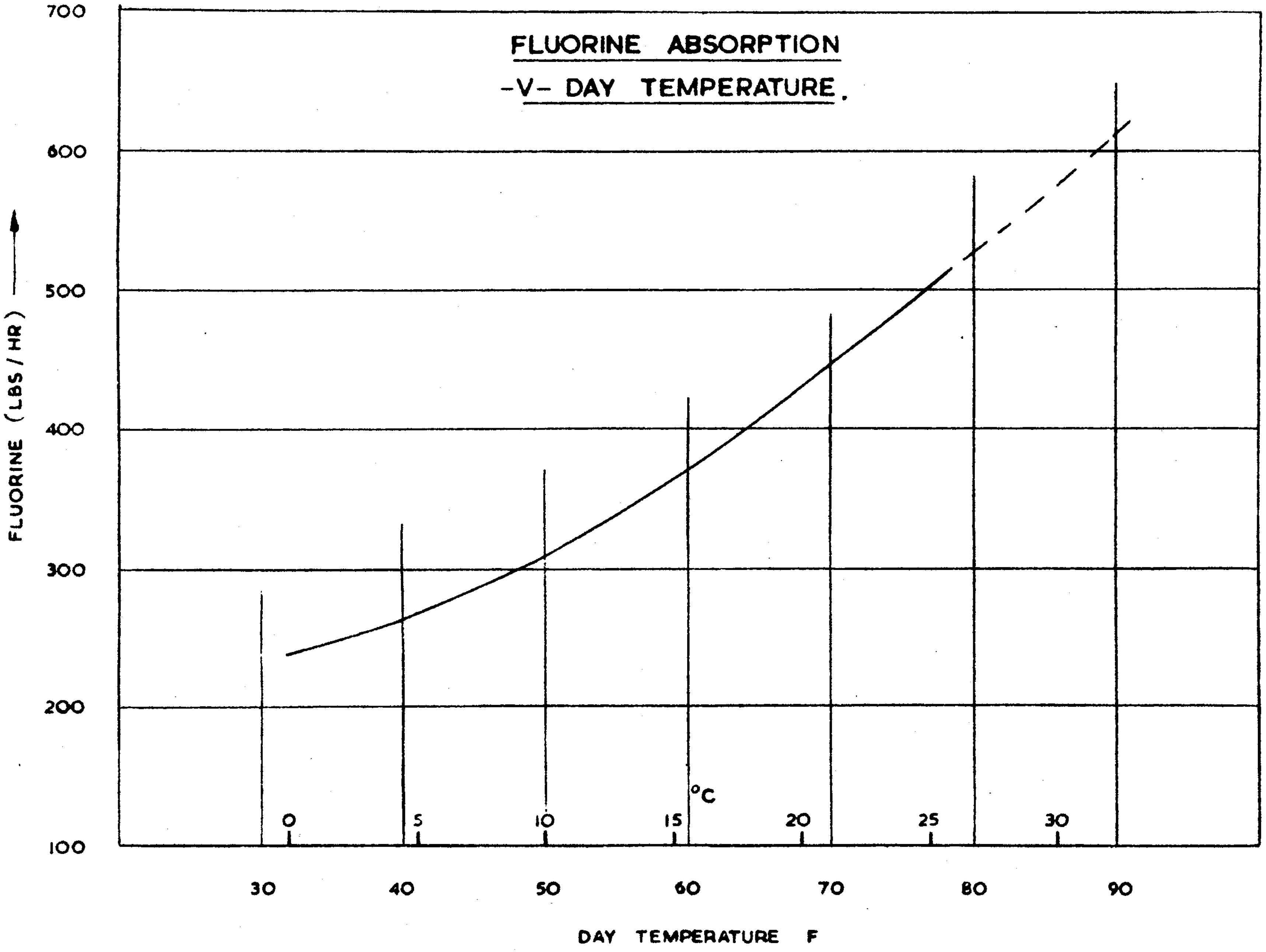

FLUORINE ABSORPTION
-V- DAY TEMPERATURE.
FLUORINE (LBS / HR)
700
600
500
400
300
200
100
°C
0
5
10
15
20
25
30
30
40
50
60
70
80
90
DAY TEMPERATURE F

FIG. 1.

AVERAGE MONTHLY TEMPERATURES & FLUORINE ABSORBED.

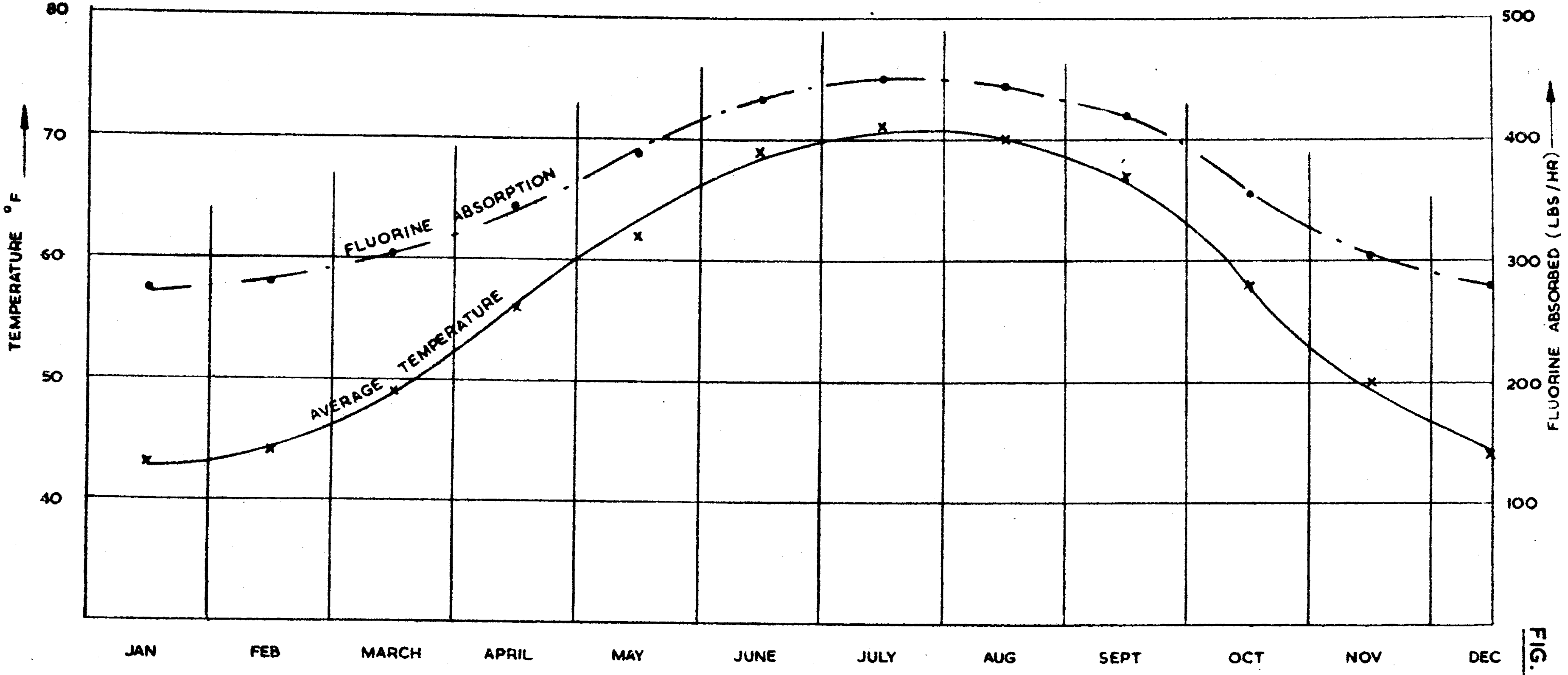
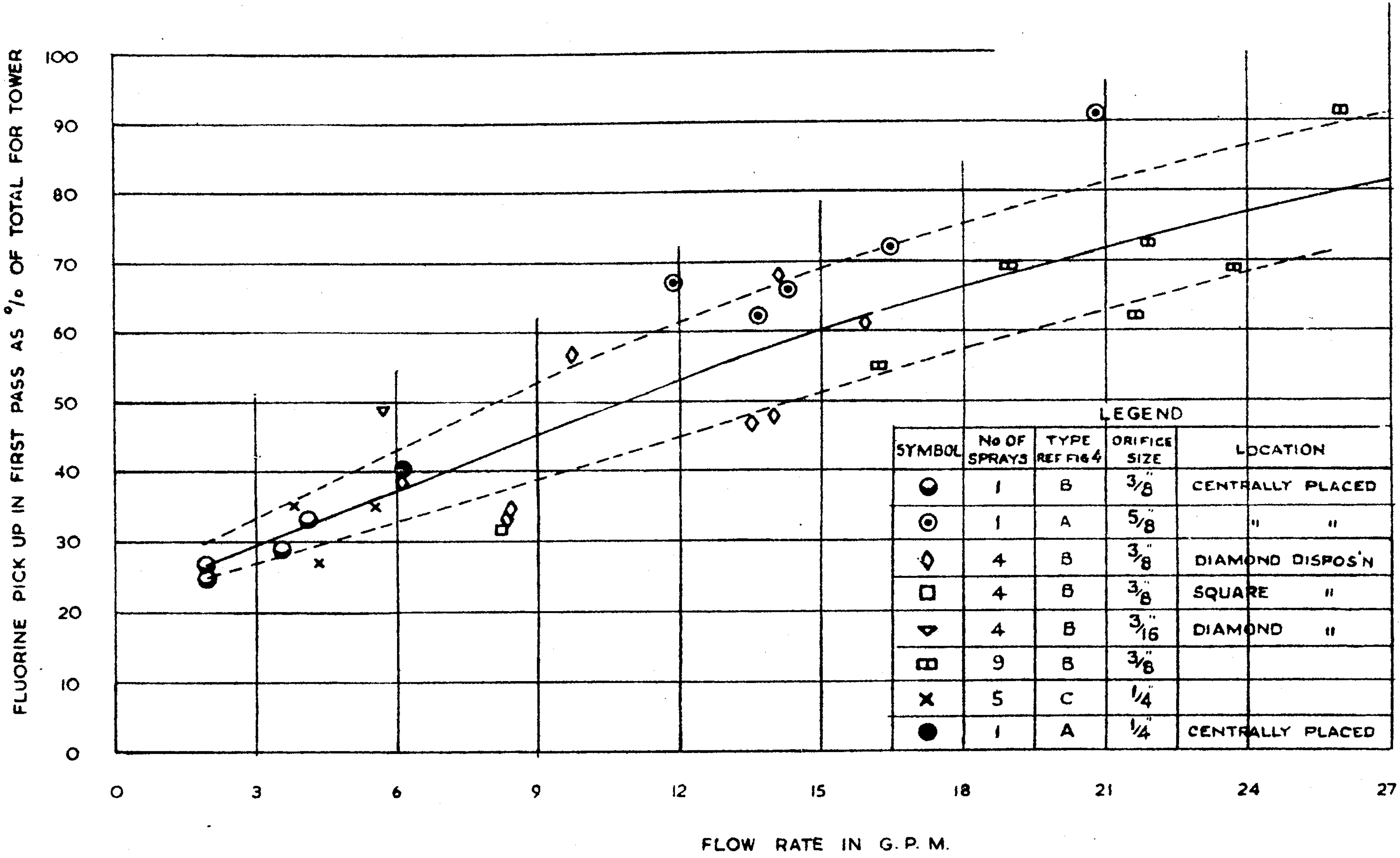


FIG. 2.

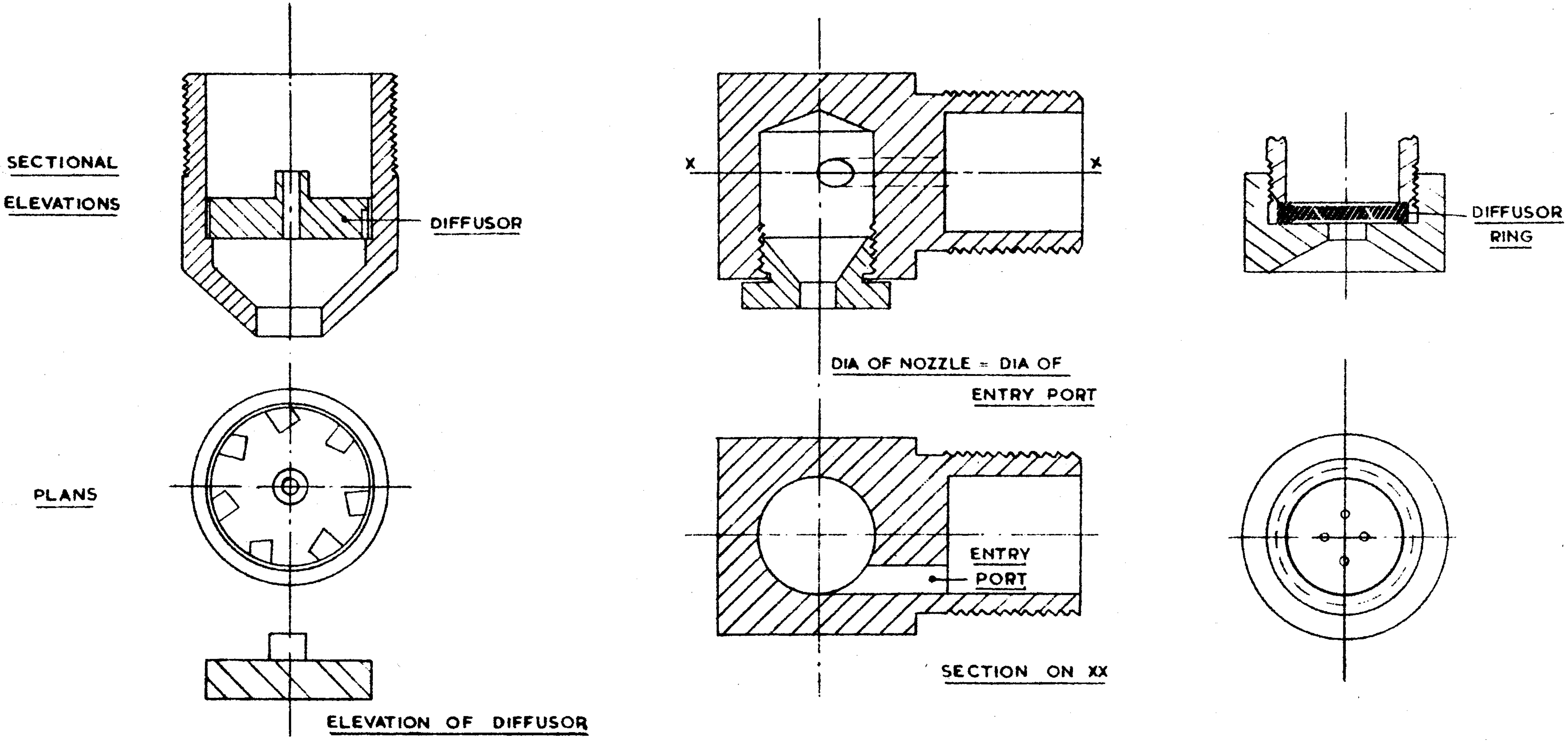
PERCENTAGE FLUORINE PICK UP AGAINST LIQUID FLOW RATE ON A SINGLE PASS. (7′ x 7′)



SYMBOL	No OF SPRAYS	TYPE REF FIG 4	ORIFICE SIZE	LOCATION
◒	1	B	3/8″	CENTRALLY PLACED
⊙	1	A	5/8″	" "
◊	4	B	3/8″	DIAMOND DISPOS'N
□	4	B	3/8″	SQUARE "
▽	4	B	3/16″	DIAMOND "
⊞	9	B	3/8″	
×	5	C	1/4″	
●	1	A	1/4″	CENTRALLY PLACED

FIG. 3.

TYPES OF SPRAYS.



TYPE A.

TYPE B.

TYPE C.

FIG. 4.

VARIATION OF RATE OF FLUORINE ABSORPTION
WITH ACID CONCENTRATION.

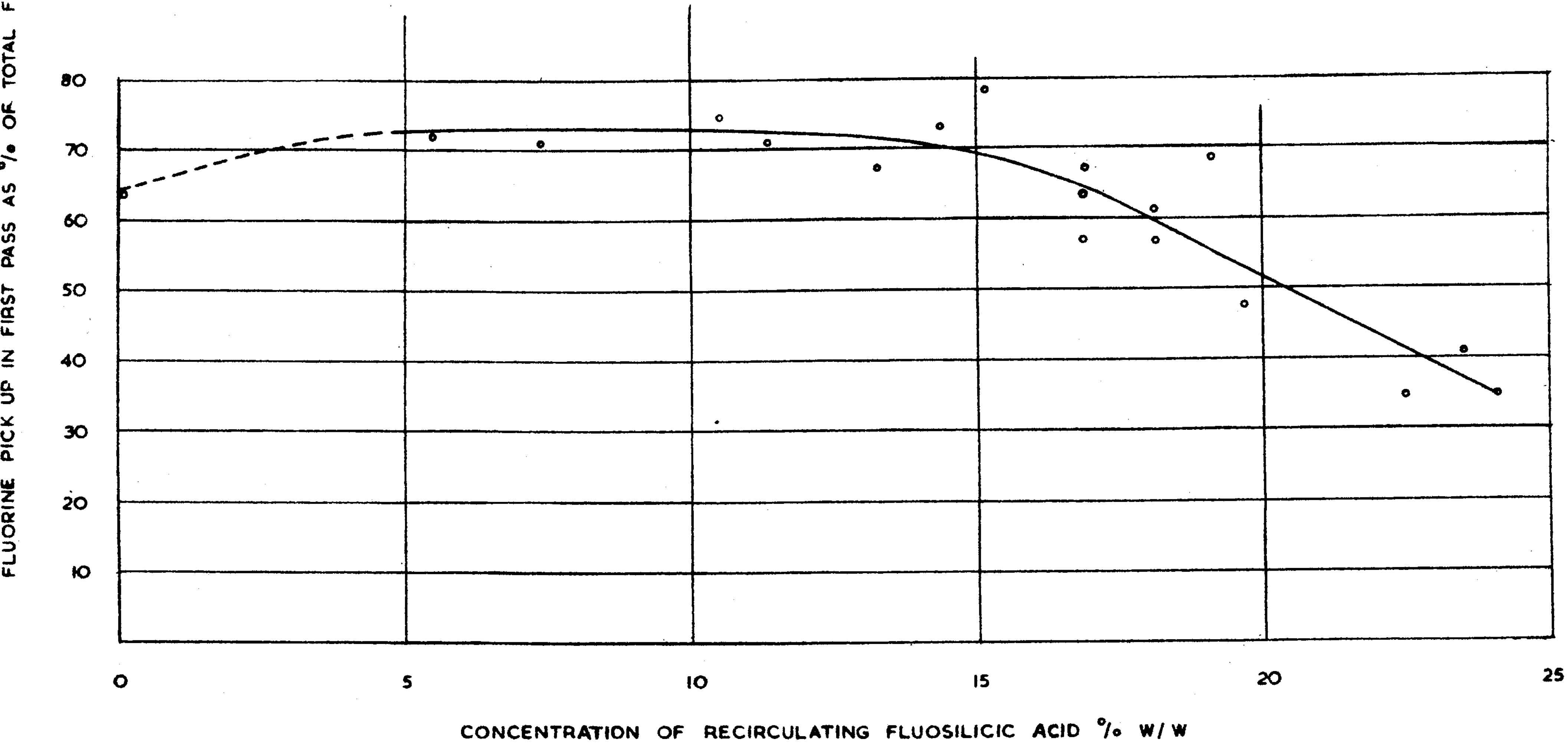


FIG. 5.