

Fluorine Absorption Coefficients in Superphosphate Den Gases

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ABSTRACT

In the manufacture of superphosphate by the acidulation of phosphate rock with sulphuric acid, fluorine is evolved, mainly as silicon tetrafluoride, along with carbon dioxide and steam. This environmentally unacceptable fluoride is required to be removed before being vented to the atmosphere. This is usually done by absorbing the gas in water. However, industrially the absorption is complicated by the presence of entrained phosphate rock dust, mist particles and condensing steam in the gas stream, and by the silica formed from the reaction between silicon tetrafluoride and water.

The absorption of dry silicon tetrafluoride in water under laboratory conditions is reasonably well understood. However, information on the absorption under industrial conditions is lacking. In all industrial measurements of the mass transfer coefficient the liquid-gas interfacial area is not known accurately and hence what is usually obtained is a coefficient per unit volume of the absorption equipment. This value is of limited use in exploring the effect of particulates and surface reaction as it is a complex average for different drop sizes and scrubber volumes and the chemical composition of the gas stream. Gas absorption, particulate collection and surface reaction need to be considered separately in comparing industrial scrubbers. Therefore in order to be able to translate the performance of a given scrubber from one works to another, the measurement of the mass transfer coefficient for one standard geometry in industrial conditions is needed. Thus the aim of this work is to establish a method of providing this information.

By using a spinning cup sampling apparatus we were not only able to establish a method of determining a mass transfer coefficient for the absorption of the industrial effluent gas stream fluorides, but were also able to establish a method for determining the size of the particulate fluorides present in the gas stream.

The main points arising from this work include:

(1) The absorption is "gas" phase controlled (under normal conditions surface silica is unimportant) and the particulate fluorides in the gas stream will often be the controlling factor in scrubber performance. Thus the collection of particulate fluorides must be a primary concern in scrubber design, and high liquid to gas ratios in some section of a scrubber will promote this collection.

(2) The particulate fluorides are small, of the order of 2 micrometers in diameter.

(3) In the spinning cup apparatus used in this study, the mass transfer coefficient for a "gas" stream containing 25% particulate fluorides at 90 to 100 °C is approximately 55 m h^{-1} .

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Section 1

INTRODUCTION

The emission of fluorides into the ambient air has long been a concern of many people. With the increased awareness of the effects of fluorides on vegetation growth and human and animal health more interest has been shown recently in the reduction of atmospheric pollution created by fluorides. The accepted threshold limit value for human exposure under industrial conditions is 3 ppm. However atmospheric pollution normally would involve concentrations far below this level.

This work deals with the fluorides emitted from the fertilizer industry in the manufacture of superphosphate. In particular the absorption characteristics of the effluent fluoride gases are studied.

Section 1-1

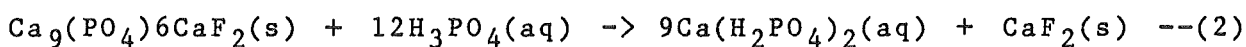
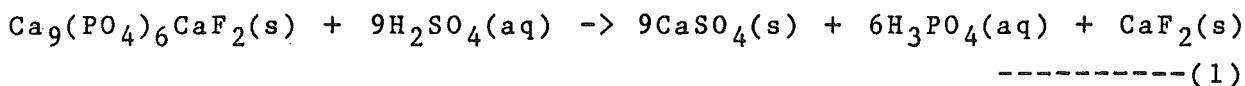
Background and Description of Study

In the manufacture of superphosphate, ground phosphate rock is acidulated with sulphuric acid, of concentration in the range 65-75%. The two principal reactions involved are:

1. The reaction of sulphuric acid with phosphate rock forming phosphoric acid and calcium sulphate.

2. The reaction of the liberated phosphoric acid with residual rock to form mono-calcium phosphate. (It is from this form that the plants are able to assimilate the phosphate.)

Since the major constituent in most phosphate rock is fluoroapatite ($\text{Ca}_9(\text{PO}_4)_6\text{CaF}_2$) then these reactions can be represented by:



Reaction (1) is rapid and is virtually completed in the mixing stage of the operation. Reaction (2) proceeds at a much slower rate with the greater part of the reaction completed in the hardening phase or "denning" of the superphosphate paste. The completion of this reaction occurs during the storage of the material which may take up to a month. This phase of the operation is known as "curing".

There are several types of units used for the mixing and denning phases of the operation. However in New Zealand all the fertilizer works use Broadfield units. These units (Fig. 1-1a) consist of a horizontal paddle mixer situated above a slow moving enclosed conveyor belt, the den. The raw materials, ground phosphate rock, concentrated sulphuric acid and dilution water are fed into the mixer and are mixed in about one to three minutes forming a slurry. This slurry then drops into the den where it reacts further and hardens as it moves along on the conveyor, taking about twenty to sixty minutes. The superphosphate is then cut out of the den using a rotary cutter,

conveyed to the granulation plant, granulated and stored prior to sale.

In addition to the two major reactions taking place in the acidulation of phosphate rock, a number of side reactions also occur due to the impurities in the rock. The reaction of particular importance in this work give the fluorides evolved in the acidulation. The fluorides are evolved as silicon tetrafluoride. The amounts and reactions involved are discussed in section 1-2.

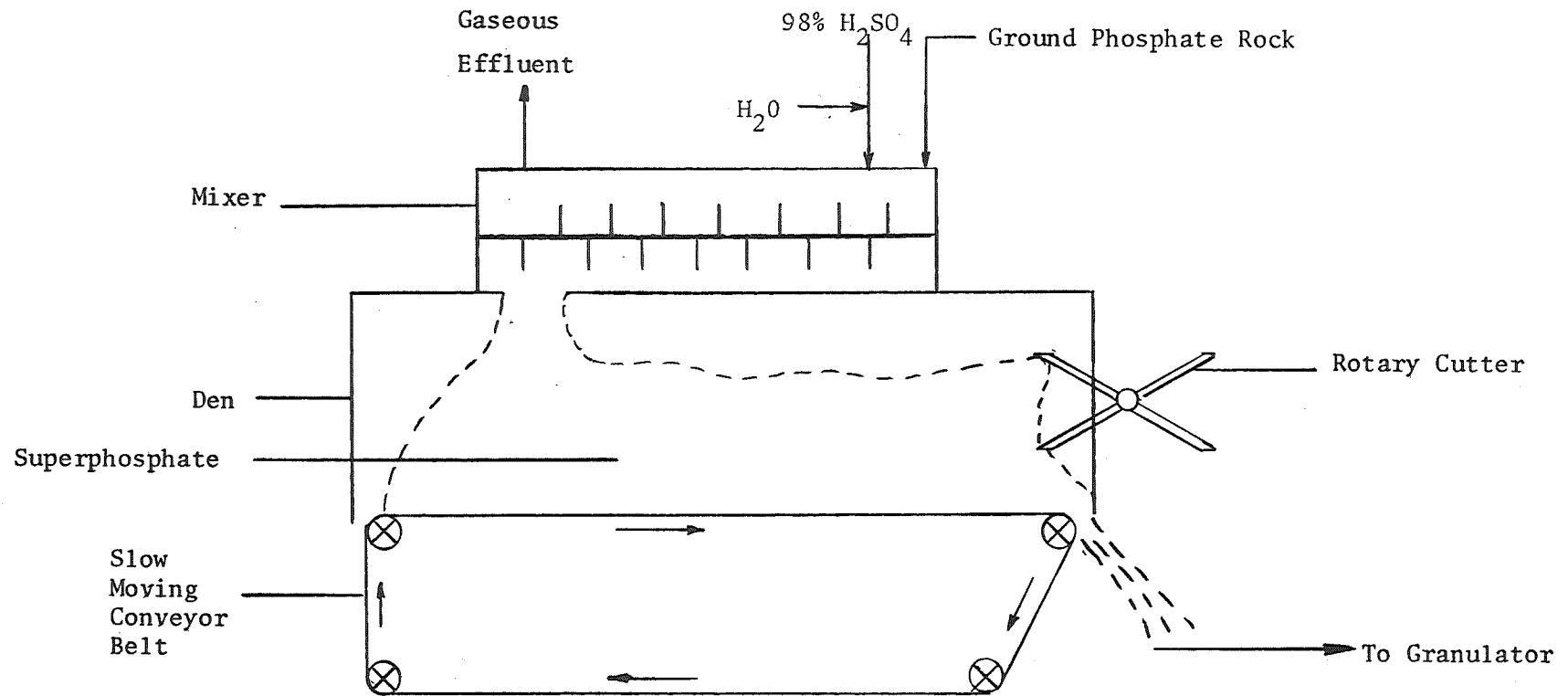
Since most of the fluorides are evolved in the mixing and denning phases of the operation air is pulled over these reacting phases and the silicon tetrafluoride along with the other gases evolved, namely carbon dioxide and steam, are carried to the gas scrubbers where the silicon tetrafluoride is required to be removed before being discharged to the atmosphere. Therefore reducing or eliminating a serious health hazard. Also, depending on the configuration of the superphosphate mixer and effluent gas ducting, and the velocity of the gas stream in the vicinity of the rock and sulphuric acid inlets, some ground phosphate and sulphuric acid droplets may be entrained in the effluent gas stream. This along with the tendency of the silicon tetrafluoride to form mist particles in the gas complicates the absorption (section 1-3).

The absorption of silicon tetrafluoride is usually achieved by scrubbing the gases with water, obtaining solutions of fluorosilicic acid and/or a higher silica fluorosilicic acid; however other processes have been used. For example, sodium carbonate solutions have been used instead of water in order to obtain sodium fluoride from which synthetic cryolite can be prepared (30). However because water is most commonly used to clean the gases, only its use will be considered in this work. The reactions of silicon tetrafluoride and water and the problems involved are discussed in section 1-3.

It has been shown (22, 41) that the absorption of dry silicon tetrafluoride in water is gas phase controlled. Whynes (41), using a wetted wall column, determined an absolute value

for the mass transfer coefficient, k_g , for the absorption. This varied from 3.9 to 45.8 m h^{-1} for linear gas velocities relative to the column ranging from 0.34 to 7.52 m s^{-1} . Koval et al (22) determined a value of k_g of 253 m h^{-1} for the absorption into water droplets of 4.1 mm diameter falling at a rate relative to the gas of 9 m s^{-1} . However these values apply to the absorption of dry silicon tetrafluoride at close to room temperature, which does not match the conditions at a fertilizer works. At most works the steam evolved is enough to saturate the effluent gases. The temperature of the gas stream may be anywhere between 50 and 100 °C as it enters the scrubber, depending on the operating conditions at the works. The gases contain particulate matter (mist particles, entrained phosphate rock). All these factors are believed to affect the mass transfer rate of the silicon tetrafluoride in the industrial situation and it was for this reason that an investigation was begun to determine an absolute value for the mass transfer coefficient at a particular fertilizer works. The aim being to develop a portable piece of apparatus that can be placed directly into the effluent ducting allowing the determination of the mass transfer coefficient easily. Such a piece of apparatus would be of help to engineers wanting to modify a gas scrubber to cope with the increasing restrictions on the levels of fluoride allowed to be discharged to the atmosphere and also for the understanding of why an existing scrubber may not be working to the required efficiency. This will become crucial as the higher fluoride-evolving phosphate rocks, such as North Carolina and Florida rocks, replaces the Christmas Island and Nauru Island rocks used in our fertilizer works. The use of collective data from existing plants will also allow a better estimate of the coefficient, than is currently available, for the design of new scrubbers.

Fig. 1-1a Broadfield Mixing and Denning Unit

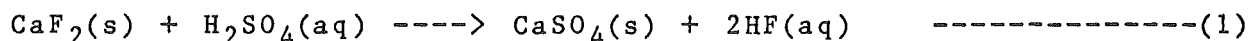


Section 1-2

The Evolution of Fluoride

As outlined in the previous section, in the manufacture of superphosphate from the acidulation of phosphate rock with sulphuric acid, fluoride is evolved, primarily as silicon tetrafluoride. The reaction mechanism leading to its evolution has puzzled researchers for a great number of years and the answer is still not well defined. However the evolution is obviously related to the nature of both the "fluoride" and the "silica" in the rock.

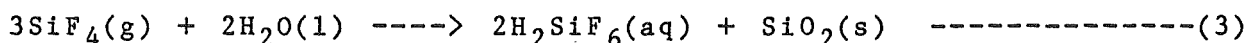
The traditional view (37, 39) of the mechanism is that the fluoride present in phosphate rock, which is primarily fluorapatite ($\text{Ca}_9(\text{PO}_4)_6\text{CaF}_2$), is present as calcium fluoride. At the temperatures found in superphosphate manufacture calcium fluoride is attacked by sulphuric acid to form hydrofluoric acid and calcium sulphate.



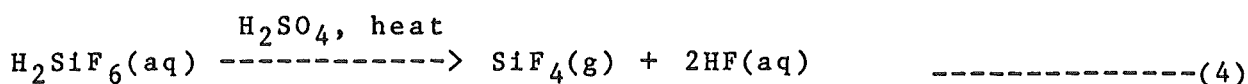
Most of the hydrofluoric acid acts upon the silica or metal silicates present in the rock to form gaseous silicon tetrafluoride and water.



The silicon tetrafluoride gas is decomposed by the water present with the formation of fluorosilicic acid and precipitating silica.

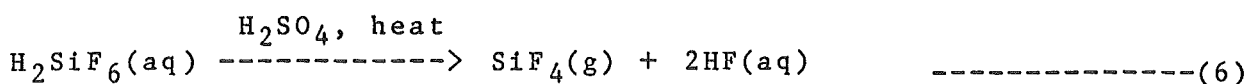
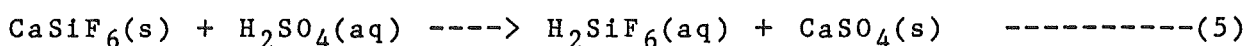


Before this last reaction takes place, however, a considerable amount of silicon tetrafluoride escapes as a gas. The fluorosilicic acid also decomposes to silicon tetrafluoride and hydrofluoric acid in the presence of sulphuric acid or at high temperatures and especially when air is blown into the solution.



This mechanism is puzzling however, in that the fluoride evolved is usually only a percentage of that contained in the rock, with an observed maximum of approximately 30% evolved, even for rocks containing more than enough silica to allow all the fluoride to be evolved as silicon tetrafluoride. This raises the question of the availability of the fluoride and silica present during the acidulation reactions.

Fox (11, 12, 13) also questioned this long accepted mechanism and proposed that the fluoride originally present in the phosphate rock is in the form of a fluorosilicate and in the acidulated rock as fluorsilicic acid. The reactions therefore being:



The evidence he gave for this was that

(1) The bulk of the fluoride evolution as silicon tetrafluoride occurs on contact between the rock and acid solutions, whereas reactions of moderately strong hydrofluoric acid with silica and many silicates are usually rather slow. This prompt and rapid evolution experienced in practice seems more consistent with the direct formation of silicon tetrafluoride.

(2) The addition of hydrofluoric acid or quartz flour (in laboratory acidulations) or hydrous silica (in plant scale tests) gave no increase in the fluoride evolution from the phosphate rock as should have happened had hydrofluoric acid been an intermediate product. Whereas incorporating calcium fluorosilicate with the phosphate rock followed by acidulation resulted in an increase in the fluoride evolution proportional to the added fluorosilicate.

However, there is also conflict with this view. Hardesty (16) expressed doubt that a fluorosilicate could be accommodated in the apatite structure of the rock. Laing and White (26) found that the addition of calcium fluoride to phosphate rock followed by acidulation gave rise to higher fluoride evolution, with the proportion evolved decreasing with increasing addition of calcium fluoride. The additional fluoride evolved was attributed to the added calcium fluoride and the decreasing proportion was believed to be related to the availability of silica in the acidulation.

In a recent article by Laing (24) on the relationship between fluoride evolution and the silica content of a number of grades of Florida and Jordanian phosphate rocks, he found that the fluoride evolution increased to a maximum of 25-35% of the stoichiometric limit related to fluorine content as both the total silica and soluble silica contents of the rocks increased, with the evolution appearing to be more closely allied to the soluble silica content than to the total silica content. Laing observed that for rocks with soluble silica contents less than approximately 1% the fluoride evolution was less than the maximum (i.e. 25-30%) and by adding precipitated silica to these rocks to bring them up to this level the evolution increased to the maximum. No further evolution was achieved for rocks with soluble silica contents above approximately 1% which is believed to be related to the availability of "fluoride" in the evolution reactions. This levelling off of fluoride evolution for precipitated silica contents of approximately 1% was also observed by Devereaux (9).

The addition of siliceous materials to phosphate rocks low in silica, such as Nauru Island and Christmas Island rocks, has been used industrially to maximise the fluoride evolution in order to produce fluorosilicic acid for sale.

Even with further silica addition to the rock the amount of fluoride evolved is still low (in the region of 30%) and this is believed to be due to the availability of fluoride in the acidulation reactions, as mentioned previously. It has been found (3, 10, 40) that the presence of acid soluble iron and aluminium in phosphate rocks lowers the amount of fluoride

evolved due to the iron and aluminium preferentially forming stable complexes with the fluoride in the superphosphate mix. White (40) has identified these complexes made from the phosphates of Nauru Island, Christmas Island and their blends and Queensland Duchess to be insoluble iron and/or aluminium fluorophosphates.

Therefore for rocks with the same silica contents but differing iron and aluminium contents different amounts of fluoride are evolved. Rocks low in iron and aluminium give relatively high evolutions, with the fluoride not evolved reacting in the superphosphate mix with the calcium phosphate component of the rock to form calcium fluoride. In contrast, rocks high in iron and aluminium evolve less fluoride, with the remaining fluoride forming calcium fluoride and/or iron and aluminium fluorophosphates.

It is also known that rocks high in fluoride and silica contents such as Florida evolve large amounts of fluoride. However, in blends with Christmas Island rock this evolution is depressed (23). This is believed to be due to the rapid dissolution of the crandallite/millisite components of the Christmas Island rock, providing iron and aluminium species in solution to complex the fluoride, thus forming iron and aluminium fluorophosphates.

It therefore appears that the evolution of fluoride is not only dependent on the amounts of fluoride and silica present in the rock but also on its chemical nature in the acidic solutions of the superphosphate mix, i.e. its availability to react.

Other factors which affect the evolution of fluoride are the processing conditions:

(1) The concentration and temperature of the sulphuric acid: In general the higher the acid strength and hence temperature the more fluoride is evolved (11, 25). The temperature is considered to be the primary effect as at high concentrations the reaction between phosphate rock and sulphuric acid is slower due to the blinding of the rock particles by the calcium sulphate formed (25).

(2) Rock fineness and Acid-rock ratio (A/R): These have a minor effect on the fluoride evolved (11, 12, 25). In general the more finely ground the rock and the higher the degree of acidulation (higher A/R) the more fluoride is evolved.

(3) The amount and type of rock dust entrained in the gas stream available to react with the fluoride gases: This is not truly a factor affecting the evolution of fluoride in the acidulation reactions of phosphate rock, as it occurs in the gas phase above the superphosphate mix. But because of its effect on reducing the fluoride levels in the gas stream, and hence entering the scrubber, it is considered an important factor. The reaction occurring between entrained phosphate rock dust, silicon tetrafluoride and water vapour has been described by White (40). The reaction leads to the formation of calcium fluoride and $\text{Ca}_4\text{AlSiSO}_4\text{OHF}_{12}\cdot 12\text{H}_2\text{O}$. This latter compound is structurally similar to the mineral chukhrovite ($\text{Ca}_4\text{SO}_4\text{AlSiF}_{13}\cdot 10\text{H}_2\text{O}$), with the sulphate necessary for its formation being provided by sulphuric acid droplets entrained in the gas stream. The reaction occurs at temperatures above 80°C . Laboratory investigations have shown that the effectiveness of the rock dust as an absorbent of the gaseous silicon tetrafluoride to be proportional to the iron and aluminium contents of the rock, with the percentage of fluoride removed by the addition of various rock dusts to the gases above the acidulated mix of Queensland Duchess rock ranging from 33% for Nauru addition to 93% for Christmas 'C' addition (5). This effect was also confirmed on a works trial where high iron/aluminium Christmas 'A' rock dust was fed into the gas stream above the mixer with the fluoride levels being reduced by one third, as measured using isokinetic sampling of the gas stream.

In summary, it can be stated that the evolution of fluoride, although not completely understood, is complex and depends on the composition of the rock, the processing parameters (i.e. acid concentration, temperature, rock fineness and A/R) and also on the concentration and equilibrium between various species (i.e. Fe, Al and SiO_2) in the liquid phase of the superphosphate mix.

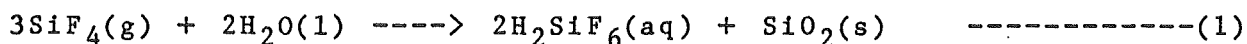
In New Zealand most superphosphate is made from various blends of Nauru Island and Christmas Island phosphate rocks with the percentage of fluoride evolved being low, approximately 4-5% of the total fluoride in the rock. The low fluoride and silica and high iron and aluminium contents of these blends contribute to this. However, with the supplies of these rocks becoming more and more difficult it has become necessary to use phosphate rocks from other sources, such as Florida and North Carolina. The current trend being to use these rocks as blends with Nauru Island and/or Christmas Island rocks. However, the fluoride evolved from these rocks is higher, due to the higher fluoride and silica contents and also their lower iron and aluminium contents, and the fluoride evolved can be as high as 30% of the total fluoride in the rock. This results in increased loadings on the scrubbing systems and hence problems of complying with the Clean Air Regulations.

Section 1-3

The Absorption of Silicon tetrafluoride in Water

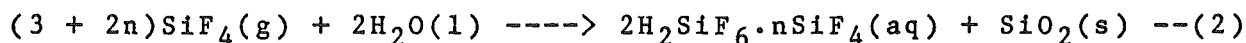
In the manufacture of superphosphate from the acidulation of phosphate rock with sulphuric acid some of the fluoride contained in the rock is evolved as silicon tetrafluoride. This environmentally unacceptable compound is removed from the effluent gases by scrubbing the gases with water. The resulting scrubber liquors are therefore solutions derived from the hydrolysis of silicon tetrafluoride. These solutions may also contain varying amounts of dissolved phosphate rock due to entrainment of some of the rock in the effluent gas stream.

The absorption of silicon tetrafluoride into water, or recirculating scrubber liquor, is accompanied by a chemical reaction with the formation of fluorosilicic acid and precipitating silica.



Tananaev (35) found however that more silicon may be present in the aqueous solution than the formula indicates giving it a lower F/Si ratio. Thomsen (36) agreed with this and found that silica-saturated fluorosilicic acid approaches a composition $\text{H}_2\text{SiF}_6 \cdot \text{SiF}_4$ which he called fluorodisilicic acid. Whynes and Dee (42) in an experiment to determine the F/Si ratio of the liquors obtained in the hydrolysis of silicon tetrafluoride, found that the liquors approximated much more closely to the complex $\text{H}_2\text{SiF}_6 \cdot \text{SiF}_4$ (F/Si = 5) than to H_2SiF_6 (F/Si = 6). Unfortunately the ratios estimated did not enable them to put forward a definite formula for the complex as complexes of the type $\text{H}_2\text{SiF}_6 \cdot \text{SiF}_4$ could also be regarded as $\text{H}_2\text{Si}_2\text{F}_{10}$ (or HSiF_5) or, if the extra silicon is present as the oxide, as $5\text{H}_2\text{SiF}_6 \cdot \text{SiO}_2$ which also have F/Si ratios of 5. Gambaretto and Pedlar (14) explain the F/Si ratio of the silica-saturated solutions as a mixture of fluorosilicic acid (H_2SiF_6) and the hydrate species $\text{SiF}_4 \cdot 2\text{H}_2\text{O}$. Another worker (19) on the solubility of silica in solutions of hexafluorosilicates proposed that the species SiF_5^- was in equilibria with $\text{SiO}_2 \cdot \text{SiF}_4$ and other fluorosilicates. Charleston (3) considered the liquors

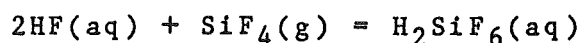
obtained from the hydrolysis of silicon tetrafluoride as being an equilibrium mixture of fluorosilicic acid and fluorodisilicic acid and he represented the liquors by the formula $H_2SiF_6 \cdot nSiF_4$, where n is determined from the F/Si ratio of the solids free liquor. The generalised hydrolysis reaction was therefore represented by the following equation.



He found, in a series of experiments using artificial scrubber liquors prepared by saturating reagent grade fluorosilicic acid with silica, that the value of n ranged from 0.46 (F/Si = 5.37) at a fluoride concentration of 1.5% to 0.55 (F/Si = 5.28) at a fluoride concentration of 12%. The temperature of the solutions, which was varied from 20 to 45 °C, appeared to have no effect on the solubility of silica and hence the F/Si ratios. Artificial scrubber liquors were used as he encountered problems in obtaining samples of works scrubber liquors free of dissolved phosphate rock. Phosphate rock is known (3) to modify the F/Si ratio of scrubber liquors by the precipitation of the excess dissolved silica over that required for SiF_6^{2-} formation. i.e. the F/Si ratio approaches 6 as the stoichiometric requirement of rock and acid is approached.

The point to note from this is that the hydrolysis of silicon tetrafluoride results in the formation of liquors with a F/Si ratio of approximately 5 (however with some doubt as to what complex(s) are formed), and that the vapour phase above such solutions consists principally of silicon tetrafluoride and water (14) unlike that from solutions without excess silica (i.e. H_2SiF_6) where hydrogen fluoride is also present (18).

A suggested mechanism for the hydrolysis reaction is given by Whynes (41) to be:



The evidence he gave for this is that (1) the direct formation of fluorosilicic acid by reaction (1) would involve the interaction of five molecules which is highly unlikely. (2) the experimental observation that glass apparatus in which the silicon tetrafluoride reacts with water becomes etched on the surface, though neither silicon tetrafluoride nor silica-saturated acid will etch glass.

The silica precipitated in the hydrolysis reaction is generally of a bulky flocculent nature, but under certain conditions it may deposit out in the form of a hard, dense scale. It is in this latter form that the main scrubbing problems result as it adheres to equipment, eventually causing blockages, and also because of its erosive nature, the life of equipment is reduced. e.g. pumps, spray nozzles, etc.

As well as the precipitating silica depositing out in the absorption equipment there is also a tendency of the silica to form a solid film at the liquid-gas interface (2, 41), which effectively reduces the rate of transfer of silicon tetrafluoride from the gas to the liquid phase. Whynes (41) and Koval et al (22) have shown that the absorption of dry silicon tetrafluoride in water can be explained by the two film theory even though chemical reaction occurs and that the gas film is controlling in the absorption, as would be expected since silicon tetrafluoride is very soluble in water. However, with the formation of a solid film of silica it is expected that this will rapidly become the controlling factor and therefore it must be taken into account when designing gas scrubbing equipment. This can be done by including in the scrubbing equipment any device capable of breaking up the silica film and exposing fresh liquid surfaces to the gas.

Calver and Hemsley (2) support this idea of creating fresh liquid surfaces. In a study of the design of void spray towers for silicon tetrafluoride absorption, they pointed out that most of the absorption occurs in the immediate vicinity of the spray nozzle, as indicated by the deposition of silica on the rim of the nozzle, and that the flowrate of liquid is important. This indicates that the reaction between silicon tetrafluoride and aqueous solutions up to the point of silica deposition is very

rapid and that the surface exposure of the aqueous solutions is one of the limiting factors.

Sherwin (33), in a study of scrubbers for superphosphate den gases, found that packed towers were more efficient than void spray towers, on a volumetric basis, which also suggests that the creation of fresh liquid surfaces is important. The longer residence time and increased liquid-gas contact area in packed towers would, however, also improve the efficiency compared to spray towers. Several other workers support the idea of the creation of fresh liquid surfaces and numerous scrubbers have been developed which are claimed to be able to handle the problems involved with silica in the absorption of silicon tetrafluoride in water.

The absorption is further complicated (33, 34, 41) by the tendency of silicon tetrafluoride to react with the condensing steam present in the gas stream to form a mist of fluorosilicic acid (or higher silica acid) together with silica as a finely dispersed precipitate according to reaction (1) or (2) above. The steam present is evolved in the acidulation of phosphate rock with sulphuric acid and is usually more than enough to saturate the effluent gases. It has been shown (14) that the vapour pressure of water in equilibrium with solutions of silica-saturated fluorosilicic acid falls off with increasing concentrations, so that as the diffusion of silicon tetrafluoride into mist particles proceeds an increase in their size occurs due to further water vapour condensation. Some of the larger particles formed settle in the gas stream ducting forming a sludge on the bottom with the remaining entrained in the gas stream. A typical composition of the sludge found in a ducting was found by Sherwin (33) to be:

	parts by weight
H_2SiF_6	25
SiO_2	5
H_2O	<u>70</u>
	100

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 where they would readily settle. This method is however unsatisfactory today with the more stringent regulations on the fluoride levels released to the atmosphere.

Because of the presence of mist particles in the gas stream, as well as particulate fluorides from the reaction with silicon tetrafluoride and entrained phosphate rock dust (section 1-2), the scrubbing system used at a fertilizer works must not only be an effective gas absorption unit, but also be capable of de-entrainment of these particulates as these are also a potential health hazard if expelled into the atmosphere. 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 (32). Not much is known about the size of the mist particles but the two-fold problem must be noted in the design of scrubbers.

The types of gas scrubbing equipment generally used in the fertilizer industry are:

- (1) Void spray chambers (both vertical and horizontal).
- (2) Spray cyclones.
- (3) Packed towers (typically low-pressure grid packing).
- (4) Venturi scrubbers.
- (5) Ejectors.

The void spray chambers are most commonly used.

Void spray chambers and spray cyclones have a relatively poor performance compared to the others and because of this several units in series are required to obtain the necessary exit gas concentrations. However, because they are essentially empty chambers problems associated with silica clogging are reduced. Spray nozzle clogging and erosion are problems however when using recirculating scrubber liquors, but these problems may be reduced by using sprays with larger portways constructed of an appropriate corrosion/erosion resistant material.

Packed towers although more efficient than spray chambers and cyclones suffer from the disadvantage of a higher gas pressure drop and a greater tendency to clog. This tendency to clog precludes any close-packed packings such as the conventional raschig rings or berl saddles etc. The most successful packings found (21, 29, 41) are the grid type which not only clog less readily but also present less pressure drop to the gas than the conventional packings.

Venturi scrubbers and ejectors offer the advantage of good contact between the liquid and gaseous phases and hence good performance, but they both suffer from high pressure drops and hence high power consumption. This power is expended, in the case of the venturi scrubber, mainly in pumping the gas and, in the ejector, in pumping the liquid. Also with these scrubbers the high velocities in the throat can result in serious erosion problems due to the silica produced, unless suitable abrasion resistant materials are used.

In New Zealand there are two types of scrubber generally used. Both are essentially void types. The first, and most common, consists of a large wooden box with internal partitioning, dividing the box into several compartments. The gas flows alternatively upward and downward through these compartments where water or recirculating scrubber liquor is sprayed. Often in the last compartment some packing is included to create a de-entrainment section. The second type of scrubber consists of a large fibreglass tower where water is sprayed in at the top and the gas flows up from the bottom. Alternating "disc and donut" type partitioning down the tower provides a "zig-zag" path for both the gas and liquid phases and hence increases the contact between the two phases. Incorporation of a packing at the top of the column is also used to increase the contact between the two phases. This type of scrubber is found better suited to handling the more concentrated liquors and the higher gas flows.

Section 1-4

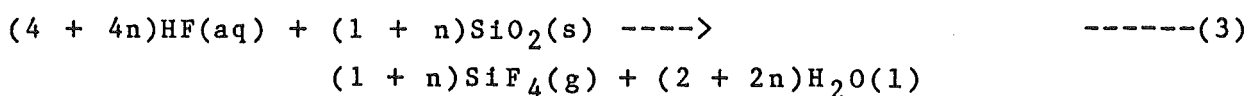
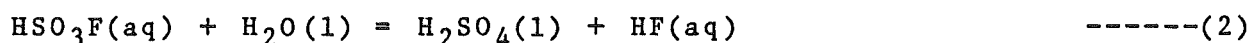
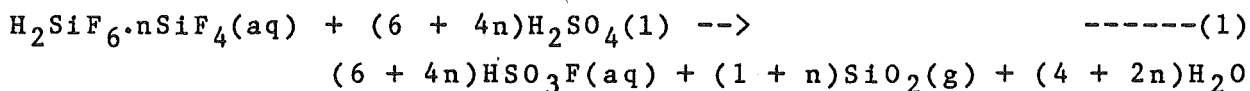
The Effect of Scrubber Liquor Recycle on the Fluoride
Levels in the Gas Stream

Traditionally the fluoride-containing liquors obtained from the scrubbing of the effluent gases have been disposed of into the sea or rivers, usually after being neutralised. However, with the ever tightening controls on the dumping of liquid effluent into such waters, as laid out by the local Catchment Boards, and with the increasing costs of neutralisation more works are investigating the recycle of scrubber liquors back to the mixer, so that these are used as acid diluent in the manufacture of superphosphate. This alternative is also appealing to those works situated inland away from any close waterways as the costs involved in disposal are also increasing by the increasing transportation costs required. Although a zero effluent discharge system like this would probably require a higher capital expenditure on scrubbing equipment, its running costs would be lower due to the elimination of scrubber liquor disposal expenses.

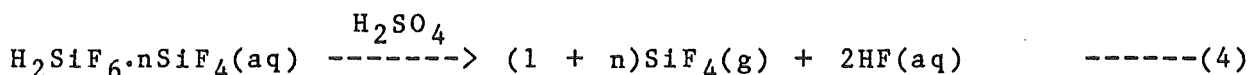
It is found (3, 4, 29) that by recycling scrubber liquor to the mixer (a zero effluent discharge system) the fluoride levels in the gas stream increase due to the re-evolution of some, or all, of the fluorides contained in the liquor. The evolved fluorine is believed to be mainly in silicon tetrafluoride. This increase in fluoride levels in the gas stream increases the loading on the scrubbing system and hence high efficiency scrubbing units are required to bring the fluoride levels discharged to the atmosphere down to those required by the Clean Air Regulations.

The amount of fluoride re-evolved has been quoted by Monaldi and Venturino (29), who have described the successful operation of a zero effluent discharge system at a fertilizer works, to be approximately two thirds of the recycled fluoride. This is equivalent to trebling the flowrate of evolved fluoride. The works used liquors of 16 to 22% fluoride to dilute sulphuric acid from 75% to 67%.

Charleston (3) in a report dealing with the feasibility of returning to superphosphate the fluoride evolved during its manufacture, proposes the following mechanism for the reaction between concentrated sulphuric acid and scrubber liquors ($\text{H}_2\text{SiF}_6 \cdot n\text{SiF}_4$). The decomposition reaction is believed to occur in three stages viz:



with the overall reaction proceeding:



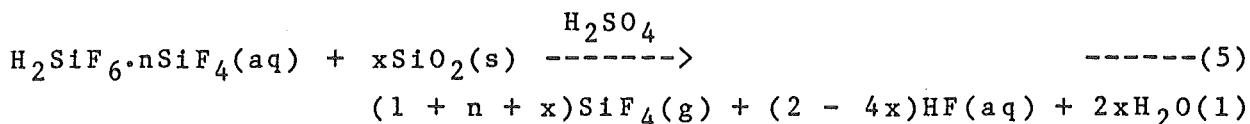
By assuming that all the silicon present in the scrubber liquor is volatilised as silicon tetrafluoride and that all the fluoride left after silicon tetrafluoride formation remains in the superphosphate then the stoichiometry of the overall reaction (equation (4)) can be used to predict the amount of fluoride re-evolved during acid dilution.

Charleston in a series of laboratory scale experiments found with scrubber liquors of fluoride concentration 3-9%, free of suspended silica [$\text{F}/\text{Si}(\text{mole}/\text{mole}) = 5.64$] and used to dilute sulphuric acid from 98% to approximately 70%, that the fluoride re-evolved showed no apparent correlation with the total fluoride levels in the liquor. The re-evolution rates were all approximately 75%, which agreed well with the 71% predicted from the F/Si ratio in the scrubber liquor (equation (4)). The type of rock used in the manufacture also appeared to make no difference to the amount of fluoride re-evolved.

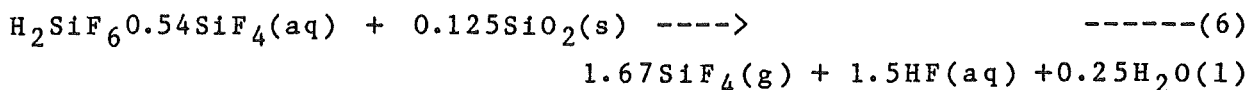
He found, however, that for scrubber liquors free of suspended silica, with varying F/Si ratios ranging from 5.3 to

6.0, that the re-evolution rate was intimately connected with the F/Si ratio. The lower the ratio, or the higher the silicon content, the more fluoride was re-evolved. When the total scrubber liquor (solid + liquid) was used as acid diluent, having a F/Si ratio of 4, he observed that virtually all the fluoride was re-evolved (~96%). This is expected as the extra silicon incorporated in the liquor as precipitated silica (section 1-2, reaction (2)) is able to react with the hydrogen fluoride produced in reaction (2) above to form silicon tetrafluoride which is evolved into the gas phase.

For a F/Si molar ratio of 4 the amount of precipitated silica present per mole of solids free scrubber liquor ($\text{H}_2\text{SiF}_6 \cdot n\text{SiF}_4(\text{aq})$) must be half a mole ($x = 0.5$). Therefore in order to predict the amount of fluoride re-evolved when some, or all, of the solids are returned with the liquor ($0 \leq x \leq 0.5$), when used as acid diluent, the following equation can be used, provided the assumptions given above in using equation (4) are made.



For example, when a solids free scrubber liquor F/Si molar ratio of 5.3 ($n = 0.54$) along with a quarter of the precipitated silica formed in the gas scrubbing ($x = 1/8$) is used as acid diluent, then the reaction occurring would be:



The amount of fluoride re-evolved would therefore be approximately 82%.

Works trials at two New Zealand works (6, 8) have in fact found that fluoride re-evolution is in the range 60-85% when scrubber liquors were used as acid diluent. The varying amounts of re-evolution were attributed to the varying F/Si ratio (solid + liquid) of the liquor recycled and the unsteady conditions at

the fertilizer works making accurate analysis difficult.

It was also observed that the recycling of scrubber liquors increases the temperature of the gas above the superphosphate mix and hence in the effluent gas stream. This increase was found to be dependent on a number of factors such as the recycle rate and the operation of the scrubbing system (i.e. the volume recirculated through the system). Temperatures as high as 100 °C have been encountered as the gases enter the scrubber.

In summary, when scrubber liquors are used as sulphuric acid diluent in the manufacture of superphosphate, the amount of fluoride re-evolved as silicon tetrafluoride is independent of the overall fluoride levels in the liquor and the type of rock used in the manufacture. The controlling factor is the amount of silicon recycled in the liquor to the mixer, i.e. the F/Si ratio of the total scrubber liquor (solids + liquid). For solids free scrubber liquors the amount of fluoride re-evolved is approximately 75% when used to dilute sulphuric acid from 98% to 70%.

Because of the increase in fluoride levels in the gas stream when using scrubber liquor recycle, it is important to be able to design scrubbers able to cope with the increase and hence an accurate value for the mass transfer coefficient under these circumstances is required.

Section 1-5

Hornby Fertilizer Works Operation

All on-site experimentation for this work was carried out at the Ravensdown Fertilizer Company Limited, Hornby, Christchurch, during the period January to December 1983.

At this works phosphate rock is converted to superphosphate at a rate of approximately 30 tons per hour in a Broadfield mixing and denning unit. Phosphate rocks from Nauru Island, Christmas Island and North Carolina are used in various blends in the manufacture. The gases evolved are extracted from a position on top of the den and are carried to the scrubber in a fibreglass-reinforced polypropylene duct (0.76 m diameter, 30 m long).

The gas scrubber (Fig. 1-5a) is a void spray type, constructed of "treated pinus", partitioned into eleven void compartments and one packed compartment, arranged for downward gas flow in the first, then alternatively upward and downward flow, with the gas leaving the top of the last compartment. Two stages of liquor recirculation operate within the scrubber. The first liquor stage incorporates the first eight void compartments and the second (weak) liquor stage incorporates the next three. The last compartment has 100 mm plastic mini-rings in the lower section and is irrigated by make-up water. The make-up water is thus added to the weak liquor sump from where a pump recycles the excess fluoride liquor to the Broadfield mixer for sulphuric acid dilution. The strength of the liquor recycled is usually less than 6.0% fluoride.

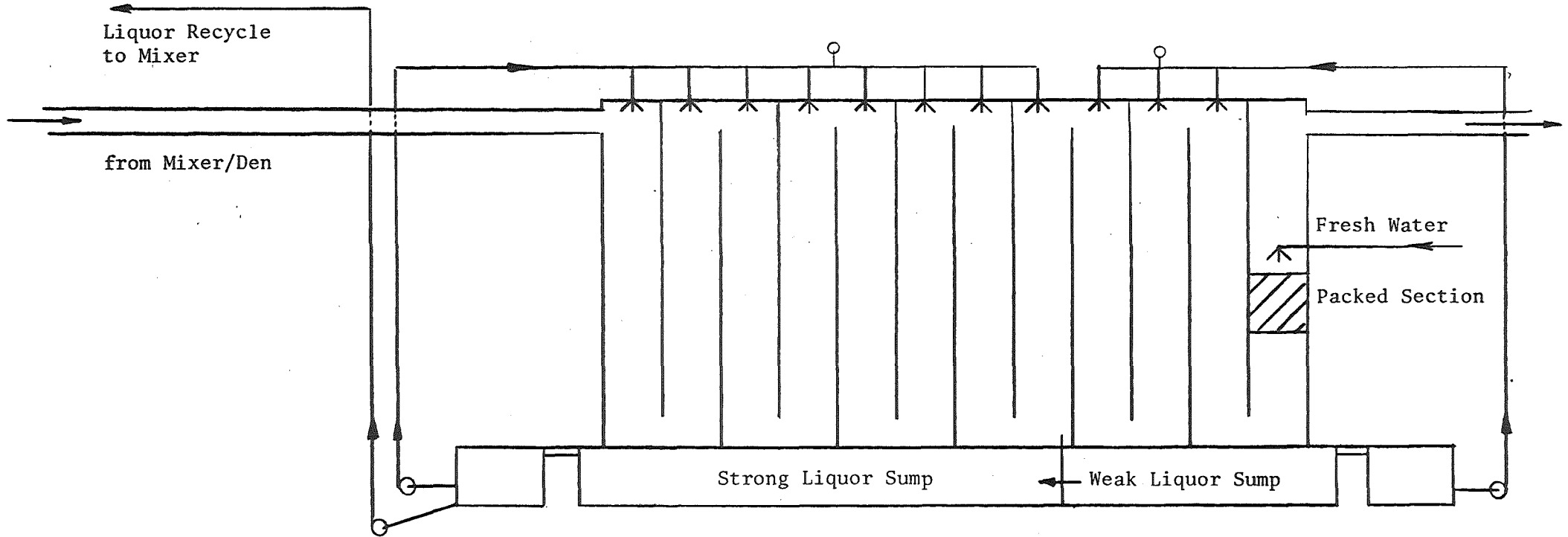
In each compartment, liquor or make-up water is sprayed by one teflon spiral nozzle (120° spray angle, full cover). There is also provision for total or fresh water spraying by connection of the recirculation spray manifold into a fresh water line.

Typical operating conditions for a 1:1 Nauru Island:
Christmas Island rock blend are:

Mixer	Rock rate	= 27.5 t h ⁻¹
	Acid rate	= 15.8 t h ⁻¹
	Recycle rate	= 84 l min ⁻¹
	Secondary water rate	= 26 l min ⁻¹
	Acid strength (after dilution)	= 68.3%
Scrubber	Strong liquor recirculation rate	= 1392 l min ⁻¹
	Weak liquor recirculation rate	= 351 l min ⁻¹
	Make-up water rate	= 85 l min ⁻¹
	Gas flow rate (dry air, 0 °C)	= 22608 m ³ h ⁻¹

The main operating problems with the scrubber and connecting pipe lines handling the gases and liquors are those caused by silica buildup and clogging, and high liquor and gas temperatures. These create problems with pumps, spray nozzles and pipe lines in the form of corrosion and erosion and also in maintaining liquor flows.

Fig. 1-5a Hornby Scrubber System



Section 2

MASS TRANSFER COEFFICIENT DETERMINATION FOR THE ABSORPTION OF
SILICON TETRAFLUORIDE IN WATER UNDER INDUSTRIAL CONDITIONS

This section deals with the design, development and testing of a piece of apparatus from which an absolute value of the mass transfer coefficient can be determined under the conditions prevailing at a particular fertilizer works. The importance of this value is to help the design of suitable gas scrubbers, for the fertilizer industry, able to cope with (a) the increasing restrictions on the levels of fluorides allowed to be discharged to the atmosphere, and (b) with increased levels of fluorides in the effluent gas stream, caused by using scrubber liquors as acid diluent and using higher fluoride evolving rocks in the superphosphate production (sections 1-2 and 1-4).

The mass transfer coefficient for the absorption of dry silicon tetrafluoride in water, under laboratory conditions, has been determined by Whynes (41), using a wetted wall column, and Koval et al (22), using water droplets. Both workers found that the absorption is gas phased controlled, as expected from the water solubility of silicon tetrafluoride, and that the mass transfer rate is hindered if the silica produced in the hydrolysis reaction is allowed to form a stable film coating the liquid surfaces. These observations have been noted industrially (2, 33). It is believed, however, that the presence of other compounds in the industrial effluent gases and the higher temperatures encountered will affect the mass transfer rate, and hence the use of the data obtained by the above workers may prove inaccurate for the design of gas scrubbers.

Industrially it is very difficult to obtain a value for the mass transfer coefficient (k_g), since the overall absorption rate observed for scrubbing equipment is a product of a mass transfer coefficient, a concentration difference and an area (A) where the area, in most cases, is not known accurately. Hence what is usually measured is $k_g \cdot A$, which is a complex average for many different size drops over different times through the scrubber volume and the chemical composition of the gas stream. Because

of this complex average comparison of a given scrubbers' performance between different fertilizer works is difficult due to the uncertainty of whether the area component is the same between the scrubbers (i.e. A) or whether the chemical composition of the gas stream entering the scrubbers is the same thus affecting the value of k_g . Therefore in order to know this a measurement of k_g for one standard geometry in industrial conditions is needed. Thus the aim of this work is to establish a method of providing this information.

The experimentation for this work was carried out at the Ravensdown Fertiliser Company Limited, Hornby, Christchurch. (A brief description of the works operation is given in section 1-5). The sampling position in the effluent gas stream was approximately 2 m upstream from the scrubber inlet.

Section 2-1

Description of Apparatus

In order to determine an absolute value for the mass transfer coefficient for the absorption of silicon tetrafluoride in water, under industrial conditions, the apparatus used must have the following characteristics:

- (1) A measurable quantity of absorbing water.
- (2) A known liquid-gas interfacial area.
- (3) A means of contacting the gaseous and liquid phases.
- (4) A means of bringing the absorbing water up to the gas temperature, before absorption, to avoid condensation of the water vapour in the gas stream and to avoid any unknown temperature effects on the absorption rate.
- (5) A means of avoiding contamination of the absorbing water from sludge running down the bottom of the gas stream ducting, produced from the reaction between silicon tetrafluoride and condensing water vapour, which may be randomly entrained in the gas stream and move as "slops" down the duct.
- (6) Compactness, so that the apparatus can be transported easily to the site so that it can be placed in the standard sampling port (100 mm (4 inch) diameter).
- (7) It must be resistant to the corrosive nature of fluoride compounds and the high temperatures.
- (8) It must have a simple flow geometry to allow some analysis of the flow, and generalisation of the results.

The apparatus designed to fulfill these requirements is shown in Fig. 2-1a. It consists of a rotating cylinder with a centrifugal blower at one end and a small lip on the other, which

is spun around on its axis by the use of a two speed electric drill (Black & Decker, model SIL23). Two cylinders are shown (Figs. 2-1b and 2-1c), as it was found (section 2-4.1) that the original cylinder (Fig. 2-1b) was unsatisfactory when being used in the sampling.

The cylinder, which will be referred to as the sample cylinder, is loaded with a known volume of water, while it is spinning, where it forms a liquid film on the inner surface, held there by the centrifugal forces exerted on it. This forms the absorption surface which has a known surface area, determined from the dimensions of the sample cylinder and the water volume used. The filter arrangement, shown, slides back and forth on the shaft. This allows the liquid film to be brought up to the temperature of the gas, once the apparatus is placed into the hot effluent gas stream. This is achieved by closing the filter so that the solid plate supporting the filter, referred to as the cover plate, is up against the open end of the sample cylinder, sealing the contents of the cylinder from the gas stream and allowing the water film to be heated, by conduction through the surrounding walls, without allowing any absorption of silicon tetrafluoride to occur. The cover plate is held in this position by the spring shown and, to a minor extent, by the vacuum created by the centrifugal pump in the sample cylinder.

Once the water film is up to the temperature of the gas, the filter is opened and locked into a stationary position. The gas is then drawn through the filter and over the water film by the action of the centrifugal pump and absorption takes place for the required length of time after which the whole apparatus is removed from the duct. The rate at which the gas is drawn over the film is dependent on the rotational speed of the sample cylinder, which can be easily varied using a suitable variac on the electric drill. The length of the sample cylinder was kept small so that the concentration of fluoride in the gas phase above the water could be considered constant throughout the absorption. Also, the liquid volume is expected to remain constant due to the gases being saturated, hence no evaporation should occur. A detailed operating procedure for the apparatus is given in section 2-1.2.

In the heating stage of the operation (i.e. when the filter is closed), the filter rotates along with the sample cylinder. This gives the filter a self cleaning action and therefore will remain relatively clean of any sludge and dust present in the gas stream, until it is required in the absorption stage of the operation. The heating of the water film also allows time for the filter to be heated to the gas temperature, thus eliminating the possibility of reaction between silicon tetrafluoride and condensed water vapour on the filter as would occur if the filter was used cold. This means that the fluoride concentration measured in the gas stream would be the same as that entering the sample cylinder.

In the absorption stage of the operation the filter is open and locked in a stationary position while the sample cylinder remains rotating. This is to avoid the gas becoming turbulent as it passes through the filter, as any turbulence in the gas stream above the water film would cause ripples to form on the film and hence surface area calculations would become difficult. Also some entrainment of the water may occur if highly turbulent gas flow exists.

Experimental observations of the water film for rotation speeds varying from 1000 to 2400 rpm showed that a smooth and stable film is formed, which is not dependent on the orientation of the apparatus. (Rotation speeds less than 1000 rpm were not tried). This allows the apparatus to be used at any angle within the duct and therefore is not dependent on the position of the sampling port. It was noticed, however, that any sudden movement of the apparatus caused some of the water to be lost and therefore to avoid this the apparatus had to be moved slowly and gently throughout the sampling.

The largest radial dimension of the apparatus, being that of the cover plate, is 80 mm and hence it is small enough to be placed comfortably in a 100 mm (4 inch) diameter sampling port.

The total length of the apparatus is approximately 450 mm (excluding the electric drill) and approximately 300 mm of this is immersed in the gas stream when sampling.

2-1.1 Materials of Construction

Because of the corrosive nature of fluorides and the high temperatures of the gases found at the fertilizer works (ranging from 25 to 100 °C) a problem arose on the materials of construction of the apparatus.

The necessity of the apparatus to be light weight, so that it can be easily handled, and the necessity of the filter arrangement to be light weight, so that the spring is capable of holding the cover plate firmly up against the sample cylinder when being used in a vertical position, ruled out the use of the known resistant metals as the main construction material. Plastics were considered ideal for this. Metals were however used for parts of the apparatus where high mechanical strength was required, in order to maintain good balance while the apparatus was spinning, such as the main shaft and the filter support rods. Stainless steel (316) was used for these parts and brass nuts were used on the filter support rods. Both these materials have been found (20, 33) satisfactory for use in fluoride absorption equipment. Stainless steel (316) was also used on the cover plate as it was considered important to have a smooth flat surface for this in order to maintain a good seal when up against the sample cylinder. The threaded plug on the cover plate used for loading and withdrawing the samples, referred to as the sample plug, was also made of stainless steel. It had been hollowed out to reduce the total weight of the cover plate. A neoprene o-ring was used between the sample plug and cover plate in order to reduce the possibility of fluoride leakage there.

At the time the apparatus was designed the temperature of the gases, at the fertilizer works as they entered the scrubber, were in the range 75 to 80 °C and therefore the plastics used in the design were chosen accordingly. Rigid polyvinyl chloride (PVC) was used on the original sample cylinder (Fig. 2-1b, section 2-1) because of its known excellent chemical resistance, high mechanical strength and low moisture absorption. Its maximum continuous service temperature in air however is in the range 66 to 74 °C which is slightly below the maximum encountered

at the works. However, because the apparatus was going to be used intermittently at these temperatures it was considered satisfactory for this purpose.

The second sample cylinder (Fig. 2-1c, section 2-1) was made of ultra high molecular weight polyethylene (UHMWPE), again because of its good chemical resistance, mechanical strength and low moisture absorption. PVC was not used as experience with the original sample cylinder showed that some distortion of the cylinder did occur under the prevailing temperatures. The UHMWPE has a higher continuous service temperature in air of 82 °C which again is on the limit of the temperatures encountered at the fertilizer works. However satisfactory use at the works for this material, as scrubber sprays and construction bolts, was found, indicating that higher temperatures could be tolerated. A heavier construction of the sample cylinder was used (i.e. thicker walls) as a means of reducing any distortion which may occur.

The bearings used were also made of UHMWPE, because of the additional property of a low coefficient of friction.

The tube and brackets used to support the filter mechanism were constructed of Tufnol, "Whale Brand". This is a cotton fabric based phenolic resin which can be used, for intermittent periods up to temperatures of 100 °C. It has good mechanical strength and chemical resistance, but, with concentrated acids (greater than ~5%), particularly at elevated temperatures, some loss in dimensional characteristics can occur. For this reason it could not be used for the sample cylinder where fluorosilicic acid is in direct contact.

The choice of plastics used on the apparatus were not only limited by their chemical, mechanical and temperature properties, but also by their availability in New Zealand. Plastics such as polypropylene and polyvinyl dichloride, which have similar chemical and mechanical properties to polyethylene and PVC, but with a higher temperature resistance (~100 °C), making them more suitable for use on the apparatus, were not readily available. The materials chosen were therefore considered the best choice

out of those locally available.

As mentioned the gas temperatures at the time of design were a maximum 80 °C. However, in the latter stages of testing the apparatus the temperatures rose to as high as 100 °C at the scrubber inlet, with an average of 96 °C. The reasons for this were believed to be due to the scrubber sump having a large build up of precipitated silica in the bottom, therefore reducing the volume of water recirculated through the system and hence attaining a higher liquor temperature. This liquor when recycled to the mixer as acid diluent boosted the gas temperature. Even with these higher gas temperatures the plastics on the apparatus maintained their dimensional characteristics.

The filter used on the apparatus was a stainless steel mesh (mesh size 11 per cm) sprung against the support rods and soldered in position, with Araldite glue coating the solder to protect it from corrosion. The glue also gave additional adhesiveness to the join.

All other joints on the apparatus were mechanically fixed - either threaded or screwed together, using brass screws.

2-1.2 Method of Operation

In all the following work a 10 cm³ sample of deionized water was used to absorb the fluorides. Syringes (10 cm³) were used to load and withdraw the samples. The drill speed was always set at 1000 rpm (i.e. the slow speed on the electric drill). This gave a gas flow of approximately 196 cm³ s⁻¹ through the sample cylinder. All sampling in the duct was conducted at a position of approximately 2 metres upstream from the scrubber inlet, with the apparatus being used in a vertical position. This enabled it to be used without continuously supporting it.

To load the apparatus for sampling, the sample cylinder was first set in motion with the filter open and locked in a stationary position. This allowed the apparatus to be placed

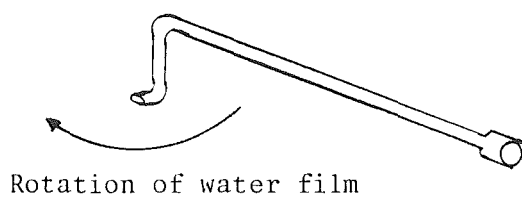
down on a flat surface. Deionized water (10 cm^3) was then carefully syringed into the sample cylinder through the hole in the cover plate and the sample plug screwed firmly into position. The apparatus was then lifted and the filter closed, care being taken all the time to avoid any sudden movements which may cause loss of some of the sample.

The sampling port was then opened and the apparatus gently placed in position in the duct. The filter remained closed for the time required for heating the water film to the gas temperature (as determined by the method outlined in section 2-4). The time was measured using a stopwatch (accuracy $\pm 0.2 \text{ s}$) with timing commencing as soon as the apparatus was seated in position, taking approximately one to two seconds from when the end of the apparatus first entered the duct. After the heating stage of the operation the apparatus was either removed from the duct, yielding a sample giving the amount of fluoride, if any, leaking into the sample cylinder during this stage, or the filter mechanism was opened and locked in the stationary position allowing absorption to take place. The timing for this stage started as soon as the filter was opened and finished when the apparatus was completely removed from the duct. To open the filter required the operator to grasp a piece of the rotating filter mechanism situated out of the duct, stop it and at the same time slide it open so that the sudden movement did not disturb the rotation of the sample cylinder. Once open the filter was locked in the stationary position.

At the required absorption time the apparatus was quickly removed from the duct with timing ceasing as soon as it was completely out of the duct. The apparatus was then gently placed down, the sample plug removed and the sample withdrawn using a syringe and placed in a plastic capped container for subsequent analysis (section 2-3.1).

The sample was withdrawn while the sample cylinder was rotating as while rotating it was possible to collect virtually all the sample. The nozzle of the syringe used to withdraw the sample was designed to reduce splashing of the sample and also so that it would not scrape the inner surface of the sample cylinder

and hence alter its dimensions. The nozzle used is shown below. The opening of the nozzle faces downstream to the water film rotation.



After each run, the apparatus was thoroughly washed down with water and spun dry. The inside of the sample cylinder along with the syringe used to withdraw the sample were rinsed three to four times with deionized water and dried with clean dry tissues to avoid contamination of further samples.

Fig. 2-1a

Mass Transfer Apparatus

(Cross section)

Not to Scale

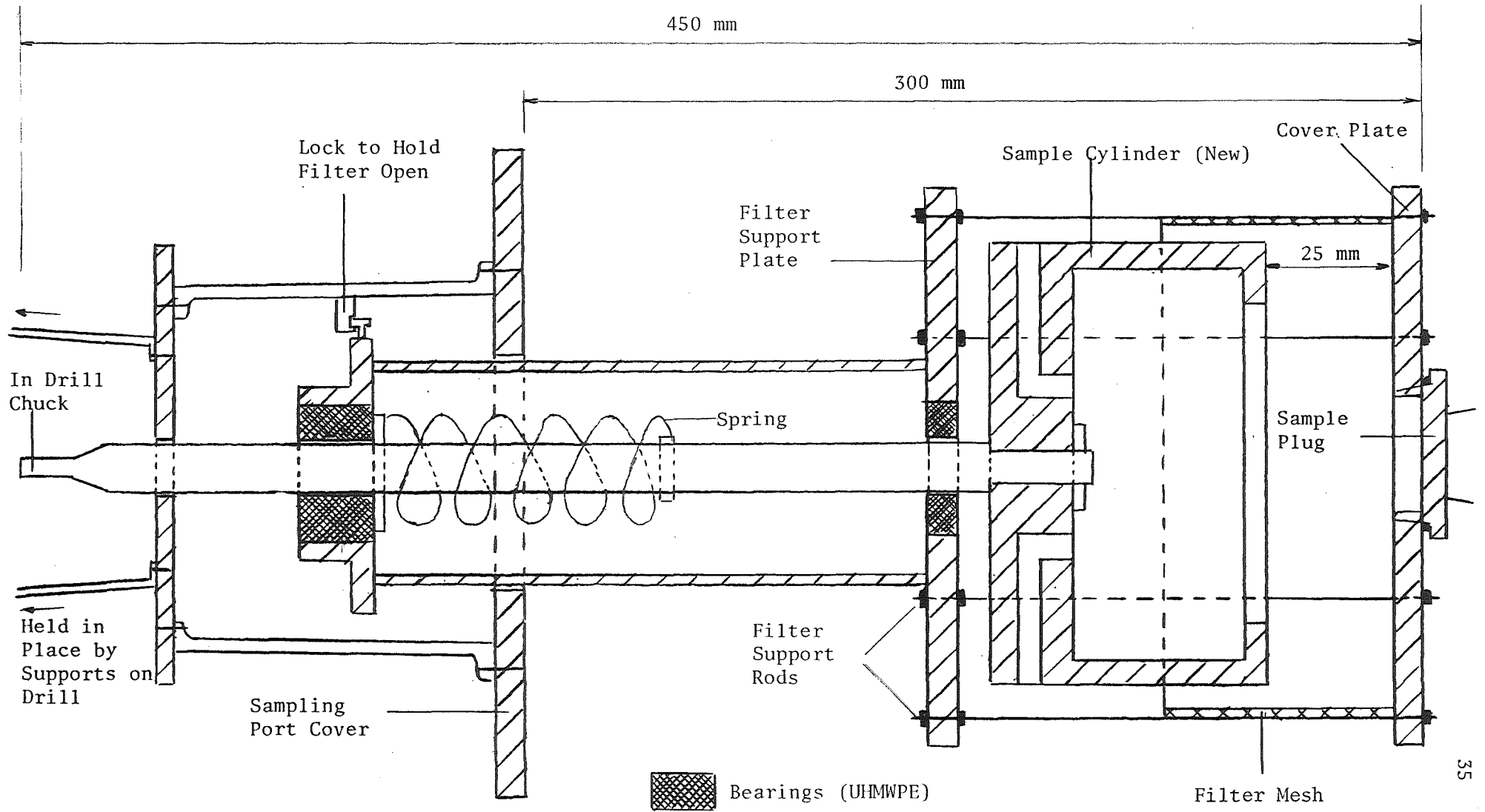
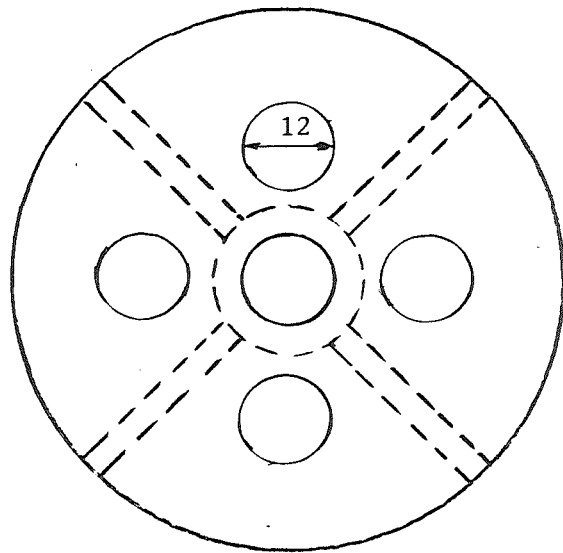


Fig. 2-1b

Original Sample Cylinder

(All dimensions in millimeters)



Section A A'

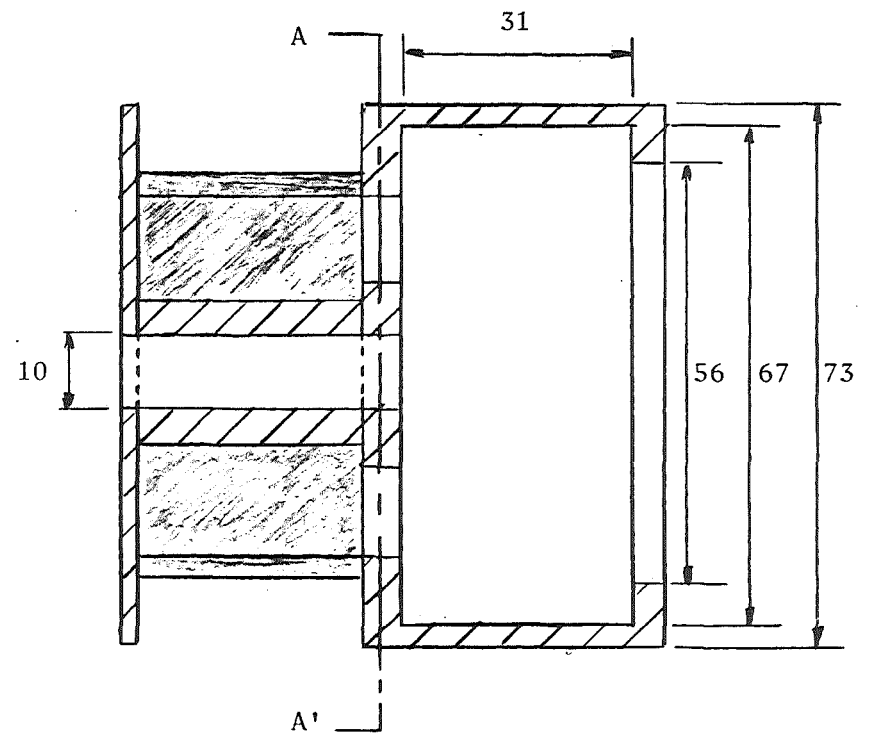
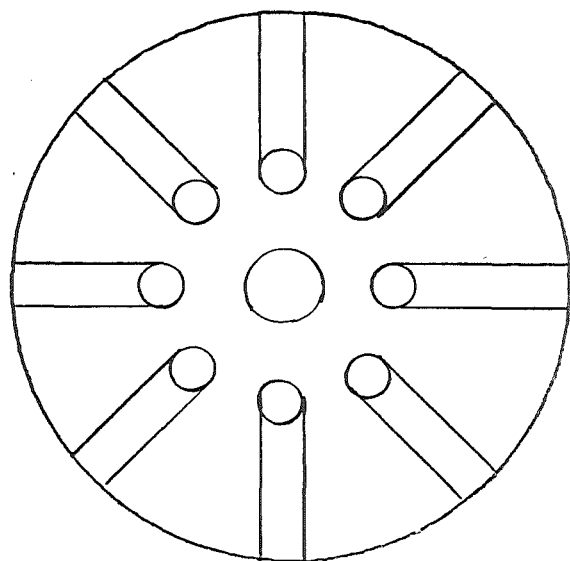
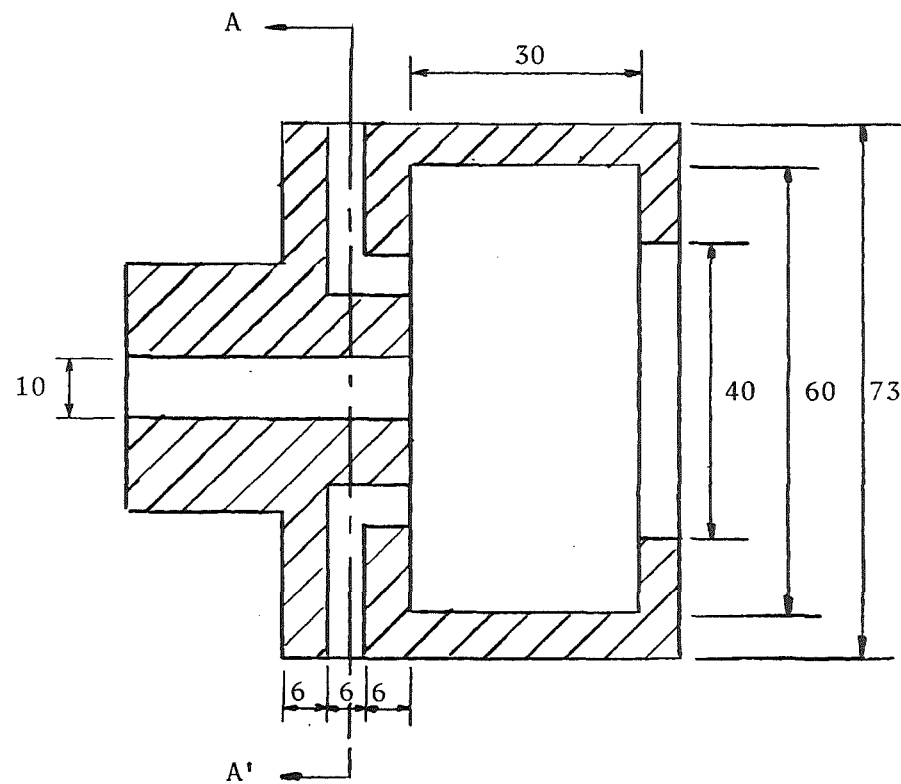


Fig. 2-1c New Sample Cylinder

(All dimensions in millimeters)



Section A A'



Section 2-2

Theory

By using the mass transfer apparatus the absolute value for the mass transfer coefficient for the absorption of "fluoride" in water can be easily calculated, at a known gas concentration and temperature, once the following assumptions are made:

(1) The gas concentration in the sample cylinder remains constant throughout the absorption and that it is completely mixed within the volume of the cylinder. The concentration being calculated from the arithmetic mean of the gas concentration entering and exiting the sample cylinder.

i.e.

$$c_{gs} = c_g - c.V/2.t.Q$$

where c_{gs} = mean gas phase fluoride concentration in the sample cylinder

c_g = fluoride concentration in the effluent gas stream

t = absorption time

c = fluoride concentration in absorption water after time, t

V = volume of absorption water used

Q = volumetric flowrate of gas through the sample cylinder = $196 \text{ cm}^3 \text{ s}^{-1}$

(2) The absorption can be described by the two-resistance theory and the gas phase resistance is controlling (as found by Whynes (41) and Koval et al (22)).

Therefore $K_g \approx k_g \ll k_l$

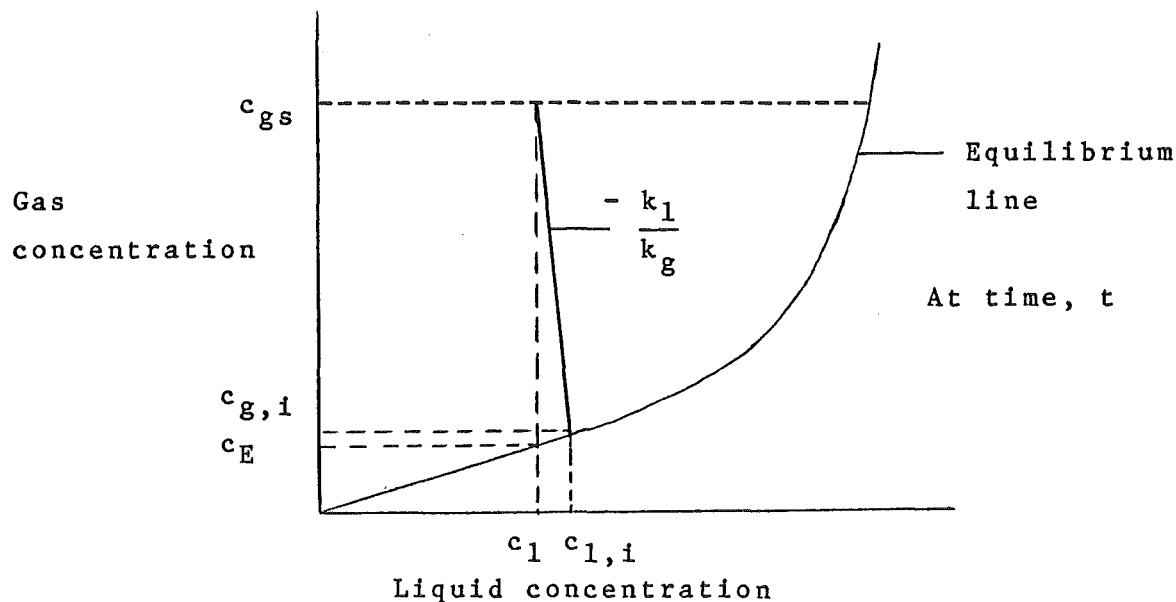
where K_g = overall mass transfer coefficient

k_g = gas film mass transfer coefficient

k_l = liquid film mass transfer coefficient

This assumption simplifies the calculation in that it can be assumed that complete mixing within the liquid film occurs and

hence the concentration of the liquid at the liquid-gas interface ($c_{1,i}$) will approximate that of the bulk liquid (c_1) and also the gas concentration at the interface ($c_{g,i}$) will approximate the equilibrium vapour concentration (c_E). This can be illustrated by the following diagram, which represents the conditions in the sample cylinder at a certain absorption time, t .



i.e. as $k_1/k_g \rightarrow \infty$, $c_{1,i} \rightarrow c_1$ and $c_{g,i} \rightarrow c_E$

(3) The mass transfer coefficient remains constant over the absorption time.

(4) The gases are saturated, hence no liquid evaporation is expected.

(5) Either (a)

The equilibrium vapour pressures above the fluoride solutions can be described by an equation of the type (section 2-2.1):

$$c_E = m \cdot c_1$$

where c_E = vapour pressure expressed in concentration units

c_1 = liquid concentration

m = Henry's Law constant, dependent on temperature

Or (b)

The equilibrium vapour pressures can be taken as being negligible.

Therefore, since the rate of absorption is given by the equation:

$$\frac{dc_{1,i}}{dt} = \frac{k_g \cdot A \cdot (c_{gs} - c_{g,i})}{V}$$

where $dc_{1,i}/dt$ = rate of change of liquid concentration at the interface ($c_{1,i}$) with time (t)

k_g = mass transfer coefficient

A = liquid-gas interfacial area

V = volume of liquid

c_{gs} = gas concentration in the sample cylinder

$c_{g,i}$ = gas concentration at the liquid-gas interface

Then, by using the assumptions (1), (2), (3), (4) and (5a) above, this can be simplified to:

$$\frac{dc_1}{dt} = \frac{k_g \cdot A \cdot (c_{gs} - m \cdot c_1)}{V}$$

and after rearranging, to:

$$\frac{dc_1}{c_{gs} - m \cdot c_1} = \frac{k_g \cdot A \cdot dt}{V}$$

This equation can now be integrated over the absorption time (t), such that;

At $t = 0$; $c_1 = c_0$ = background concentration

and at $t = t$; $c_1 = c_t$ = absorption concentration

hence, after integrating and rearranging:

$$k_g = \frac{V}{A \cdot t \cdot m} \cdot \ln \frac{c_{gs} - m \cdot c_0}{c_{gs} - m \cdot c_t} \text{-----(1)}$$

Thus allowing the determination of the mass transfer coefficient.

Alternatively, using the assumptions (1), (2), (3), (4) and (5b) above (i.e. assuming the vapour pressures are negligible), the rate of absorption of fluoride can be simplified to:

$$\frac{dc_1}{dt} = \frac{k_g \cdot A \cdot c_{gs}}{V}$$

And after integrating, using the same limits as above, the mass transfer coefficient can be determined from:

$$k_g = \frac{(c_t - c_o) \cdot V}{A \cdot t \cdot c_{gs}} \text{-----(2)}$$

Both these equations (1 and 2) will be used as a means of determining the absolute value of the mass transfer coefficient for the "fluoride" absorption in water under industrial conditions. Comparison of the results obtained from each equation will also allow the determination of the significance of the vapour pressures on the mass transfer rate.

The liquid-gas interfacial area (A), used in the equations above, can be readily calculated from the following equation:

$$A = W \cdot \pi \cdot [D^2 - (4 \cdot V / W \cdot \pi) (\rho / \rho')]^{0.5} \text{-----(3)}$$

where W = width of the water film

D = inside diameter of the sample cylinder

V = volume of water used measured at ambient temperature

ρ = density of water at ambient temperature

ρ' = density of water at gas temperature

The inside diameter (D) of the sample cylinder and width (W) of the water film are fixed by the dimensions of the sample cylinder and are $(60.0 \pm 0.1) \times 10^{-3}$ m and $(30.0 \pm 0.1) \times 10^{-3}$ m respectively. The density ratio (ρ / ρ') is included in the equation to take into account the change in volume of the water, and hence interfacial area, due to the change in temperature of the water film from when it is loaded into the apparatus to when it is at the temperature at which absorption takes place, namely the gas

temperature.

In calculating the mass transfer coefficient (k_g) all the gas phase concentrations will be expressed in units of mg F m^{-3} dry air at the actual gas temperature and all liquid phase concentrations in units of mg F m^{-3} pure water, thus allowing k_g to be expressed in velocity units (m s^{-1}) at the temperatures involved in the gas phase.

2-2.1 Vapour Pressure of Fluoride above Absorption Liquors

In any experiments involving mass transfer operations it is important to know accurately the vapour pressures of the system being studied.

Several authors have reported vapour pressure data for the F-Si-H₂O system (1, 3, 17, 27, 29). This data can be divided into two classes, those for solutions of pure fluorosilicic acid (1, 17, 27) and those of solutions of silica-saturated fluorosilicic acid (3, 29). The silica-saturated solutions, as found in scrubber liquors (section 1-3), are considered more realistic for the liquors obtained from the hydrolysis of silicon tetrafluoride and hence the vapour pressures for these solutions will be used in this work. The vapour pressure data reported by Monaldi and Venturino (29) has unfortunately been expressed in terms of F/H₂O ratios in the vapour phase. Therefore in order to use this data either the vapour pressures of water over such solutions is required, which is not available, or the assumption that the solutions behave ideally and follow Raoult's Law must be applied.

The more direct data (i.e. data expressed in units of weight of fluoride per volume of air) is that given by Charleston (3) who has determined vapour pressures of fluoride over scrubber liquors with concentrations ranging from 10000 to 140000 ppm F at temperatures from 55 to 85 °C. He has also reported the vapour pressure data for scrubber liquors with various amounts of dissolved apatite in them and found that the vapour pressure decreases with increasing amount of apatite in the liquor.

However, because the samples obtained with the mass transfer apparatus were small (10 cm^3), this did not allow the determination of the apatite content of the solutions and therefore the vapour pressure data used in the mass transfer calculations will be that given by Charleston for solutions free of dissolved apatite. Therefore the vapour pressures used will be higher than actually occurring if apatite is present in the solutions obtained and this should be born in mind when comparing the mass transfer coefficients determined by the two methods given above (equations (1) and (2), section 2-2).

The temperatures encountered at the fertilizer works, at the sampling point, for the effluent gases, and hence the water once brought up to temperature, was generally higher (aproximately 90 to $100 \text{ }^\circ\text{C}$) than the temperatures studied by Charleston (55 to $85 \text{ }^\circ\text{C}$) in determining the vapour pressures. Hence it was necessary to extrapolate his data to cover this temperature range. Analysis of his results revealed that the vapour pressures at a particular liquor concentration varied logarithmically with temperature in the range 55 to $85 \text{ }^\circ\text{C}$, which allowed least squares analysis to be used to determine a line of best fit through the data and hence enable a calculation of the vapour pressures at higher temperatures (Fig. 2-2.1a). All lines had a correlation coefficient between 99.96% and 100.00% .

From these equations the vapour pressures were then determined, for each liquor concentration, at the temperatures 90 , 95 and $100 \text{ }^\circ\text{C}$ (Table 2-2.1a, Fig. 2-2.1b). As can be seen from Fig. 2-2.1b the vapour pressures show a linear relationship with liquor concentrations for concentrations less than or equal to 60000 ppm F with an "exponential-type" increase for the concentrations above 60000 ppm F . Further analysis of the extrapolated data for concentrations less than 60000 ppm F lead to the plot, Fig. 2-2.1c, where least squares analysis was used to determine the line of best fit through the data for each temperature. All lines in this plot had correlation coefficients greater than 99.90% . Hence from this plot the vapour pressures (in mg F m^{-3} dry air @ $0 \text{ }^\circ\text{C}$) could be determined over the temperature range encountered at the works and for concentrations less than or equal to 60000 ppm F . However, in order to simplify

the mass transfer calculations a general equation as a function of both temperature and concentration was determined. This equation was determined by the following method.

Since it was found (Fig. 2-2.1a) that:

$$c_E(T) = \exp(A \cdot T + B) \quad \text{at a particular concentration, } c_a$$

where $c_E(T)$ = vapour pressure as a function of temperature

T = liquor temperature ($55 \leq T/^\circ\text{C} \leq 100$)

A, B = constants

And (Fig. 2-2.1c) that

$$c_E(c_1) = m \cdot c_1 \quad \text{at a particular temperature, } T_a$$

where $c_E(c_1)$ = vapour pressure as a function of liquor concentration

m = Henry's Law constant

c_1 = liquor concentration ≤ 60000 ppm F

Then the general equation for the vapour pressure as a function of liquor temperature and concentration is:

$$\begin{aligned} c_E(T, c_1) &= [c_E(T)_1 / c_{a,1}] \cdot c_1 \\ &= [\exp(A_1 \cdot T + B_1) / \exp(\ln c_{a,1})] \cdot c_1 \\ &= \exp[A_1 \cdot T + B_1 - \ln c_{a,1}] \cdot c_1 \quad \text{-----(1)} \end{aligned}$$

for $55 \leq T/^\circ\text{C} \leq 100$ and $c_1 \leq 60000$ ppm F

A_1 and B_1 are determined from Fig. 2-2.1a at a liquor concentration, $c_{a,1}$. Hence at $c_{a,1} = 40000$ ppm F, A_1 and B_1 are 130.7×10^{-3} and -4.90 respectively. Therefore, the general equation for the vapour pressures in units of mg F m^{-3} dry air @ 0°C , when c_1 is in units of ppm F and T in $^\circ\text{C}$, is:

$$\begin{aligned} c_E(T, c_1) &= \exp[130.7 \times 10^{-3}(T) - 4.90 - \ln 40000] \cdot c_1 \\ &= \exp[130.7 \times 10^{-3}(T) - 15.5] \cdot c_1 \quad \text{-----(2)} \end{aligned}$$

And when c_E is in units of mg F m^{-3} dry air at the actual gas

temperature (T_g), which is equal to the liquor temperature (T), the equation becomes:

$$c_E(T, c_1) = \exp[130.7 \times 10^{-3}(T_g) - 15.5][273/(273 + T_g)] \cdot c_1 \quad \text{--(3)}$$

This general equation (equation (3)) showed good agreement with the vapour pressure data read directly from the vapour pressure versus temperature plot (Fig. 2-2.1a), when converted to the same units, over the temperature range 55 to 100 °C and for concentrations less than or equal to 60000 ppm F. For the temperature range interested in, in this work (i.e. 90-100 °C) the maximum error encountered, between equation (3) and the vapour pressures read directly from Fig. 2-2.1a, was approximately 5%. This was at a concentration of 60000 ppm F and a temperature of either 90 °C or 100 °C. The accuracy of the equation is the greatest at concentrations less than 40000 ppm F or at temperatures close to 95 °C over the entire concentration range. Allowing for a 2% error in Charlestone's original data the maximum error is approximately 6.5%.

For concentrations greater than 60000 ppm F there is no simple relationship for the vapour pressures as a function of temperature and concentration and therefore all vapour pressures required in this concentration region must be approximated from Fig. 2-2.1a.

Table 2-2.1a

Vapour Pressure Data Extrapolated from Charleston's Data

Liquor Concentration c_1 , ppm F	Vapour Pressure c_E , mg F m ⁻³ dry air @ 0 °C		
	90 °C	95 °C	100 °C
10000	230	455	889
20000	471	432	1845
40000	955	1835	3528
60000	1500	2738	4998
80000	2265	4051	7246
100000	3943	7136	12918
120000	6506	11879	21692
140000	12024	22899	43610

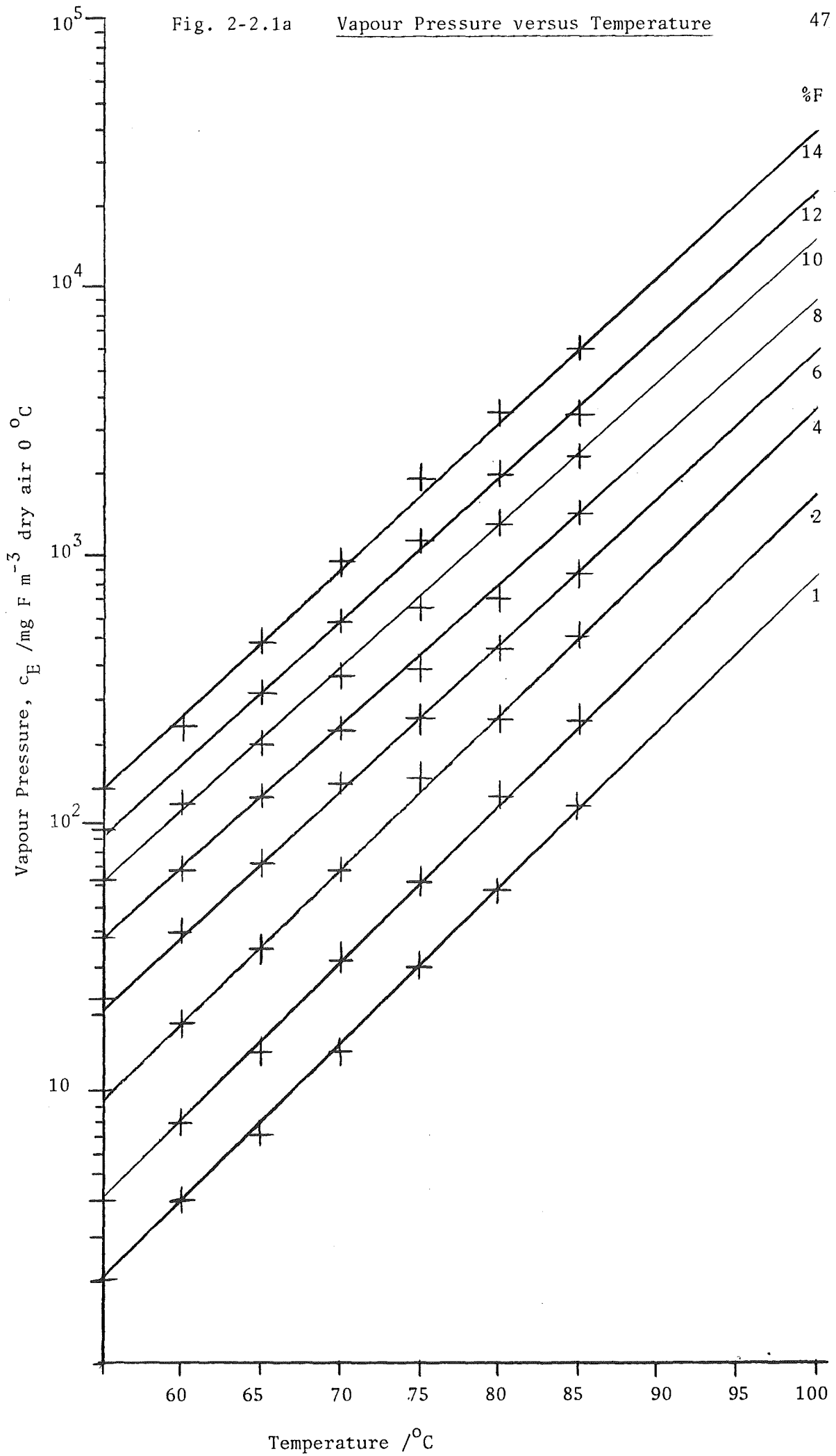


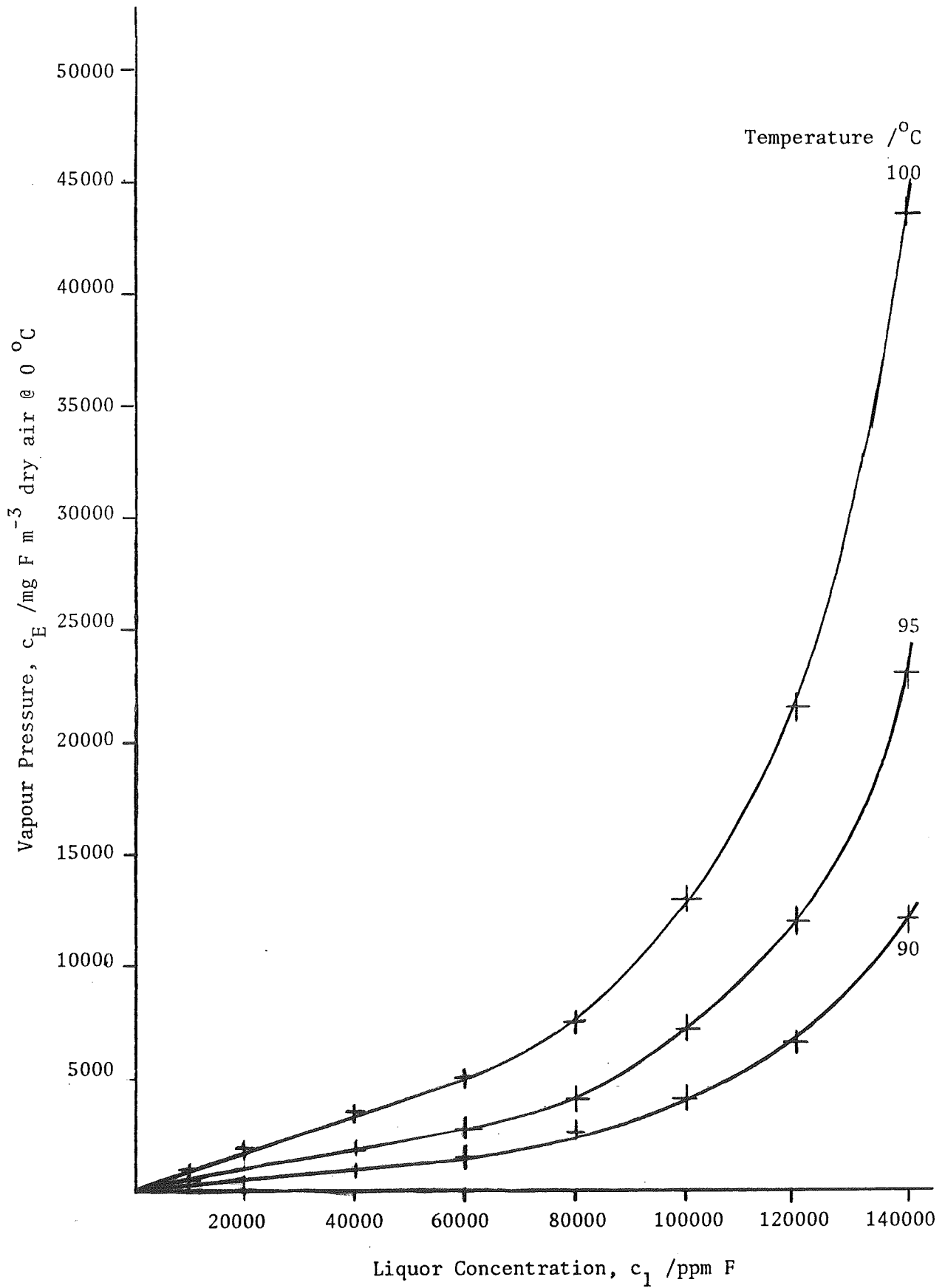
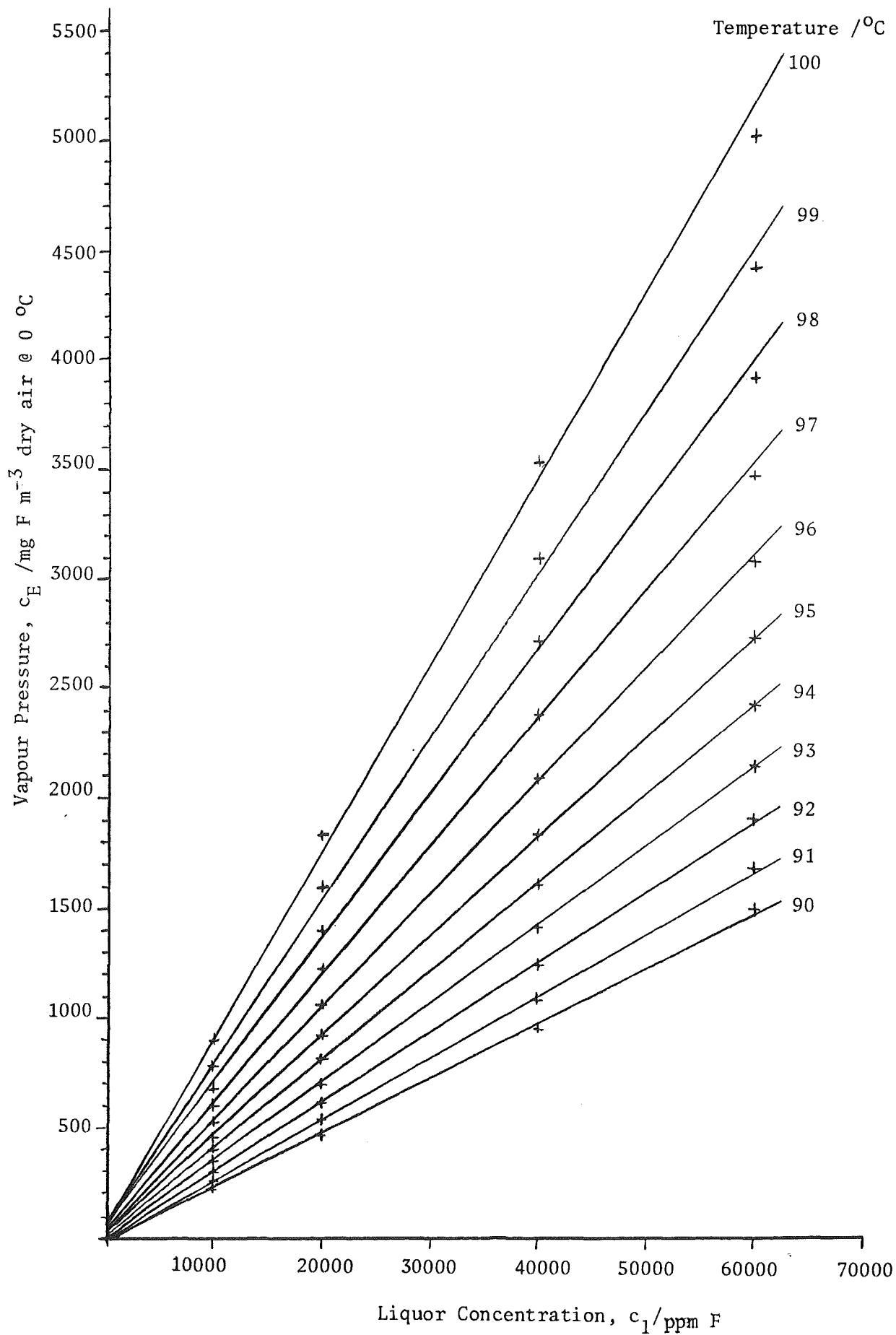
Fig. 2-2.1b Vapour Pressure versus Liquor Concentration

Fig. 2-2.1c Vapour Pressure versus Liquor Concentration

Section 2-3

Fluoride Analysis2-3.1 Fluoride in Aqueous Solutions

The method used for the determination of the fluoride concentration in aqueous solutions was that currently practised at the fertilizer works.

An Orion fluoride selective ion electrode (Model 94-09A) and an Orion single junction reference electrode (Model 90-01-00) together with an Orion specific ion meter (Model 407A) were used to perform the analysis. The advantages offered by the use of the electrode over other methods, such as alkali titration and Alizarian Fluoride Blue (A.F.B.) colorimetric method, is that it allows a number of solutions to be measured simply and quickly and is also subjected to less interference from a number of other ions which may be present in the solution.

The samples to be analysed were prepared by diluting with deionized water to obtain solutions of concentrations in the region 10 to 100 ppm fluoride. To 90 cm³ of the solutions 10 cm³ of tri sodium citrate buffer (pH = 5.6) was added in order to adjust the pH to the desired region of 5 to 6 and to maintain a constant ionic strength. The buffer used was prepared by dissolving 588.02 g of sodium citrate in 52 cm³ of 60% HClO₄ and making up to 2 litres.

Standards of 10 and 100 ppm fluoride, prepared using sodium fluoride, were used to calibrate the meter, allowing direct measurement of the unknown fluoride solutions in parts per million. Each 100 cm³ of standard contained 10 cm³ of buffer.

All fluoride solutions were stored in plastic containers and left to come to room temperature before measurement commenced. This precaution was to avoid errors associated with temperature changes affecting the electrode potentials during the measurement. Orion state in their manual that a small change in

temperature of 1 °C will give rise to a 2% error at the 10 ppm fluoride level.

During the analysis with the electrode, solutions were stirred at a constant rate not allowing a vortex to be formed, using a magnetic stirrer. A piece of "Pinex" was placed between the stirrer and the sample container so that any heat generated in the stirrer motor would not alter the temperature of the solution being analysed.

Between each measurement the electrodes were rinsed with deionised water and blotted dry with a clean dry tissue. Care was taken not to generate any static electricity on the electrodes which would affect its response and the accuracy of the result.

Generally, measurements were repeated at least twice with regular calibration of the meter. It was found that, with calibration of the meter approximately every hour, results reproducible to $\pm 2\%$ could be obtained.

2-3.2 Fluoride in Effluent Gas Stream

All gaseous fluoride concentrations were determined using isokinetic sampling with the apparatus shown schematically in Fig. 2-3.2a. This was the current accepted method practiced at the fertilizer works.

The sampling apparatus consisted of a stainless steel (316) probe, lined with ultra high molecular weight polyethylene (nozzle diameter = 3 mm), and this was connected to two polypropylene absorption cells (250 cm³ capacity), connected in series. A Thomas vacuum pump (maximum capacity 25 l min⁻¹), was used to draw the fluoride containing gases through the absorption cells, where they were absorbed in deionized water, with the gas flowrate being controlled by the cock shown, and measured using the gapmeter. An Aichi Tokei gas meter (Model K7213), accurate to ± 0.5 litres, was used to measure the volume of gas withdrawn. The gases were dried before passing through the vacuum pump and gas meter by first passing them through a container of dry silica

gel. The temperature of the gas as it passed through the gas meter was measured using the temperature gauge, accurate to ± 0.5 °C, situated at the gas meter outlet. PVC tubing was used for all connecting lines. The temperature of the effluent gas stream was measured using an alcohol-in-glass thermometer, with accuracy ± 0.1 °C.

In all sampling a known volume of gas (~20 litres) was withdrawn at an isokinetic flowrate of 4.5 l min^{-1} . The probe was placed at the same depth and position as that of the sample cylinder of the mass transfer apparatus. The absorption cells, through which the gas was bubbled to recover the fluorides, each contained approximately 100 cm^3 of deionized water. During the sampling the temperature of the gas was recorded, approximately every minute. After sampling was completed the probe and all connecting tubing up to the second absorption cell was rinsed thoroughly with deionized water and collected along with the solutions obtained in each absorption cell. The exact volume of solution obtained was measured in the laboratory and analysed for fluoride as described in section 2-3.1.

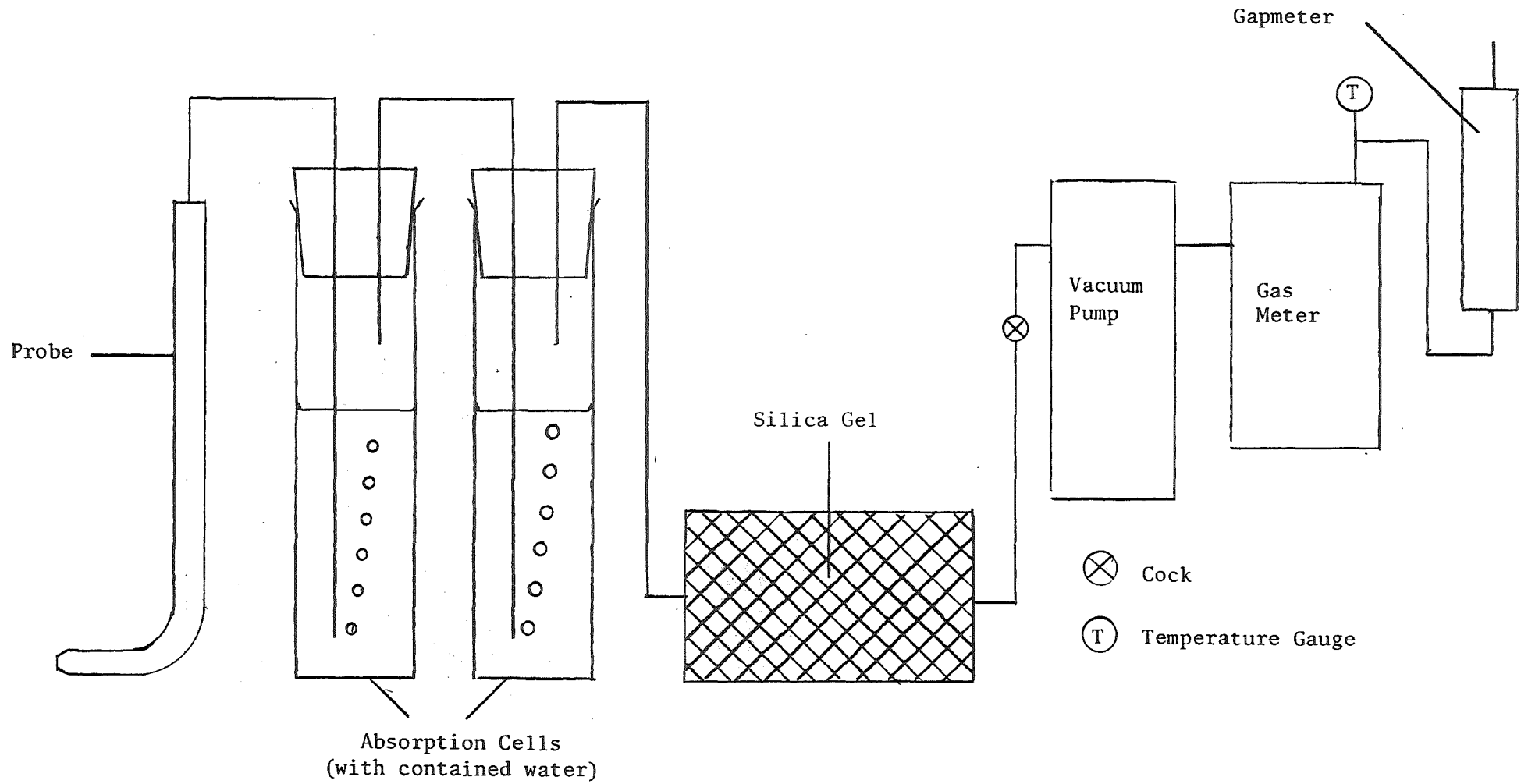
All gaseous fluoride concentrations were calculated as mg F m^{-3} dry air @ 0 °C, by the following equation:

$$c_g = \frac{c_{aq} \cdot V_{w,T} \cdot \rho_{w,T} \cdot (T' + 273)}{273 \cdot V_{g,T}}$$

where c_g = gas concentration / mg F m^{-3}
 c_{aq} = fluoride solution concentration / $\text{mg F kg}^{-1}(\text{H}_2\text{O})$
 $V_{w,T}$ = fluoride solution volume, measured at room temperature (T) / m^3
 $\rho_{w,T}$ = density of water at temperature (T) / kg m^{-3}
 T' = gas temperature at gas meter / °C
 $V_{g,T}$ = gas volume at temperature (T') / m^3

These values are readily converted to mg F m^{-3} actual air in the gas stream and when in this form are suitable for mass transfer calculations. The expected accuracy of the gaseous fluoride concentration determined by this method is $\pm 3\%$ maximum (appendix 1).

Fig. 2-3.2 Apparatus for Effluent Gas Sampling



Section 2-4

Heating the Water Film in the Apparatus

Heating the water film, formed in the mass transfer apparatus, to a temperature as close as possible to that of the gas, is required in order to avoid the condensation of water vapour contained in the gases. This, if allowed to happen, would complicate the mass transfer calculations by providing a bulk flow normal to the film.

The heating is achieved by placing the apparatus, loaded with water (10 cm³) into the hot effluent gas stream, with the filter closed and allowing time for heat to be transferred through the surrounding walls. In this stage of the operation the water is "sealed" from the gas and no fluoride absorption should take place. However, this was not the case and was the subject of several investigations.

2-4.1 Reduction of the Fluoride Absorbed During the Heating Stage

Initially when the apparatus was tested, by the method outlined in section 2-1.2, the amount of fluoride absorbed during the heating stage was excessively high (Table 2-4.1a, day 1). So much fluoride was able to "leak" into the apparatus and be absorbed that the absorption appeared not to depend on whether the filter was closed or open. This can be seen by comparing the fluoride concentrations obtained when the apparatus was operated with the filter closed for 2.5 minutes and when it was operated with the filter closed for 2 minutes and open for 0.5 minutes. Both concentrations are approximately the same. For this to be happening the fluoride concentration in the "sealed" sample cylinder must be approximately the same as that in the gas stream and for this to occur the gas must have been either leaking in between the cover plate and the sample cylinder or forced in (reverse to intended flow) through the holes of the pump (4 x 10 mm diameter).

To improve the seal between the cover plate and the sample cylinder, a neoprene o-ring was fitted to the cover plate. This however, produced no major reduction in the fluoride leakage (Table 2-4.1a, day 2). Its actual effect is difficult to determine since no tests were possible without it on the day and comparison of results between day 1 and 2 are virtually impossible, since gas concentrations are not known.

To test whether the fluoride leakage was occurring due to gas being forced in through the holes of the pump while the water film was being heated, small corks were placed in these holes. The results (Table 2-4.1a, day 2) indicate that a major reduction in fluoride leakage was obtained. However, there was still a significant leakage occurring. Some distortion of the PVC sample cylinder had also occurred before these results were obtained which may have contributed to this. The distortions probably being due to the high temperatures the apparatus was exposed to (~ 80 °C).

Because of this distortion and the significant effect of blocking off the pump on the fluoride absorption, a new sample cylinder was tried, made of a higher temperature resistant material (section 2-1.1) and having a pump with smaller holes (8 x 6 mm diameter) making the entrance for the gas more difficult. The results of tests carried out with this new sample cylinder (Table 2-4.1a, days 3 and 4) show that the amount of fluoride absorbed was reduced considerably assuming the gas concentration is approximately the same as the previous days. However, it was still considered too high for use as a background concentration in the determination of the mass transfer coefficient. From heat transfer calculations the time required for heating the water film to within two degrees celsius of the gas temperature was estimated as 14 minutes, for gas temperatures less than 99 °C (appendix 2). Therefore considerably more leakage was expected for this heating time, than that measured in these tests.

To reduce the fluoride leakage further an airway was constructed down through the centre of the shaft of the apparatus (Fig. 2-4.1a). This allowed clean air from outside the duct to be pumped through the sample cylinder during the heating stage

(rather than fluoride gas being pumped through any leaks between the sample cylinder and the cover plate) thus keeping the gas phase above the water film free of fluoride. An UHMWPE rotating seal on the shaft, situated out of the duct (Fig. 2-4.1a), with a length of rubber tubing connected, allowed a means of blowing clean air into the sample cylinder if required. The centrifugal pump on the sample cylinder caused air to be drawn through the airway at a rate of approximately $0.6 \text{ cm}^3 \text{ s}^{-1}$, as measured using a soap bubble flowmeter connected to the rubber tubing. (Cylinder rotation speed approximately 1000 rpm). This rate was increased slightly by the vacuum in the duct (approximately -0.6 kPa pressure).

The results of tests using the airway (Table 2-4.1a, days 5 and 6) indicate that the fluoride absorbed due to leakage was reduced by approximately 30% when the airway was open to the outside air. The difference in results for days 5 and 6 are difficult to explain without knowledge of the gas concentrations, however, the obvious reason is that a significant reduction in the gas concentration occurred on day 6. Further testing (Table 2-4.1a, days 7 and 8) showed that the fluoride leakage could be reduced further by blowing clean air through the airway at a rate of approximately 4.5 l min^{-1} , this achieved a reduction of approximately 35% of that obtained when the airway was blocked, or 5% more than that obtained when the airway was open without blowing. The clean air flow was created by connecting the rubber tubing of the airway onto the outlet of the vacuum pump used for the isokinetic sampling of the gases, with the flowrate measured using the gapmeter (Fig. 2-3.2a, section 2-3.2).

However, the fluoride being absorbed was still considered too great for the length of time the apparatus was in the duct (~2800 ppm F was absorbed for 2.5 minutes heating at a gas concentration of 4700 mg F m^{-3} dry air @ 0°C). For the gas to be leaking into the sample cylinder, creating such high liquor concentration, the only possible explanation was that the gas was still being forced through the holes of the pump, even though a pump with smaller diameter holes was used. This was possible since the gas stream velocity, transverse to the axis of the cylinder and aligned with the holes as they swung round

(Fig. 2-4.1a), was approximately 11 m s^{-1} . Therefore in order to inhibit the flow of fluoride gas through the sample cylinder a clean air flow greater than 18.7 l min^{-1} would be required through each hole of the pump (6 mm diameter), or a total clean air flow through the sample cylinder greater than 150 l min^{-1} would be required. There is no way that such a high clean air flow could be created with the existing apparatus as velocities greater than 350 m s^{-1} would be required in the constricted portions of the airway. Therefore what was required was some way of reducing the fluoride gas stream velocity near the outlet holes of the pump during the heating stage of the sampling. A similar problem would also be encountered when the filter was opened and the absorption was allowed to take place. In this absorption stage the gas would follow a path in at the upstream-facing holes and out at the downstream-facing holes, perhaps without travelling far along the axis of the sample cylinder (Fig. 2-4.1a). Therefore the problem was not only to reduce the gas velocity around the pump during the heating stage but also during the absorption stage. This was achieved by placing a tightly fitting piece of rubber tubing over the filter support rods (Fig. 2-4.1b) long enough to shield the pump from the gas stream when the filter was closed (heating stage) and open (absorption stage). A gap equivalent to the opening distance of the filter was left between the rubber shield and the cover plate, and a gap of approximately 10 mm was left between the shield and the filter support bracket, thus enabling gas to flow through the apparatus while the filter was open. The results of tests carried out with the rubber shield are shown in Table 2-4.1a, day 9. As can be seen a substantial reduction in the fluoride absorbed due to leakage is achieved, of the order of 85% with the airway blocked and approximately 97% when blowing clean air through the apparatus at a rate of approximately 10 l min^{-1} .

Further testing (Table 2-4.1a, day 10) showed that with the pump shielded and with clean air being blown into the sample cylinder the fluoride leakage was small, with the leakage being dependent on the clean air flowrate. However, as can be seen, there are some anomalies in these results. For example, the fluoride leakage at an airflow of 2 l min^{-1} is less than that at 3 l min^{-1} . This may have been caused by a change in the

operating conditions at the works, as indicated by the small reduction in gas temperature observed at these times. Also the air flows into the sample cylinder recorded are only approximate as some leakage of the clean air being blown into the airway was observed around the rotating seal. However, the overall effect of blowing air through the airway, on the reduction of fluoride leakage, can be seen.

Because the heating times tested so far have been no longer than 3 minutes, with the expected time being approximately 14 minutes, it was considered impractical at this stage to try to reduce the fluoride leakage any further, until the actual time required for heating was known and the consistency of the fluoride leakage at that time was known. The latter point was important because if the leakage concentration was constant then it could be readily accounted for in the mass transfer calculations.

2-4.2 Preliminary Studies of the Time Required for the Heating Stage

Some of this work was carried out concurrently with that of reducing the fluoride leakage into the sample cylinder (section 2-4.1).

Initially the time required for heating was estimated using a copper/constantan thermocouple probe with an ice point reference thermocouple, connected to a Phillips digital multimeter, accurate to ± 0.05 mV. This was done by conducting a series of experiments using the mass transfer apparatus, loaded with water (10 cm^3), and measuring the water temperature obtained after being heated by the gas stream for increasing times. The water temperature was measured by placing the probe on the inner surface of the sample cylinder as soon as possible after removing the apparatus from the gas stream. Between each test the apparatus was cleaned, cooled to atmospheric temperature and reloaded with a clean sample of water.

The experiments carried out this way, however, lead to some anomalous results and hence the actual time required for heating could not be accurately determined. The anomalies were probably due to errors created by varying heat losses possible between removing the apparatus from the duct and measuring the temperature, and also to the unsteady conditions at the fertilizer works over the long times required for such experimental tests (several hours). However, one obvious result obtained was that the time required for heating the water film was longer when air was being blown through the airway of the apparatus, than when no air was being blown through. This was determined by conducting two repeated tests, one where air was blown through the airway and the temperature was measured after 3 minutes heating time, and the other when no air was being blown through for the same heating time. The results are shown below.

Gas Temperature/°C	Heating Time/min	Air Flow /l min ⁻¹	Water Temperature/°C
90	3	4.5	62
90	3	0	73
88	3	4.5	59
91	3	0	70

This increase in heating time found when air was blown through the airway is believed to be due to the rush of cool air passing over the water film and cooling it. One way of reducing this problem was to blow hot air through the apparatus rather than cold air. This may also have increased the rate at which the water film was heated over that obtained when no air was blown through the airway, due to the water being heated from both sides of the film. This would be an advantage in that the fluoride leakage obtained would be less.

Two methods were tried to heat the air before it was blown into the sample cylinder. The first of these was simply to place a U-tube heat exchanger (4 mm ID, 6 mm OD x 2 m, stainless steel (316) tube) in the hot gas stream and to connect it in series between the air source and the apparatus. However, because of problems with heat losses through connecting tubing and the apparatus no noticeable increase in the water film temperature

was observed for each of the heating times studied (Table 2-4.2a, part A). The second method was to use a heat exchanger connected to the outlet of the airway (Fig. 2-4.2a) which heated the air just before it entered the sample cylinder, thus avoiding the problems of heat losses. The heat exchanger (4 mm ID, 6 mm OD x 600 mm (total length) stainless steel tubing) was mounted on the removable sample plug on the cover plate. The air flowed up the centre tube and back through the two returning tubes into the sample cylinder. A sprung connection between the airway outlet and the heat exchanger was used in order to provide a good connection, during the heating stage, without lifting the cover plate from the sample cylinder. Again, the results using the heat exchanger indicate that the time required for heating was still greater when the airway was used (Table 2-4.2a, part B). A possible reason for this is that the water film was being simultaneously cooled as it was being heated by the hot airflow. This was possible since the velocity of the cold air being blown through the airway in the constricted region of the shaft, where the sample cylinder was supported, was high ($\sim 21 \text{ m s}^{-1}$ @ 91 min^{-1} airflow), thus causing a high heat flow away from the sample cylinder and hence cooling the contained water. Another possibility is that air was leaking around the connector to the heat exchanger hence cold air was still passing over the water film. This is possible since it was never absolutely certain whether a good connection, between the heat exchanger and the airway outlet, had been made during each measurement.

Because of the problems encountered in reducing the increased heating time attained when using the airway, a decision on whether or not more time should be spent on improving the heat exchanger had to be made. As it stood at the time, using the airway may well lead to the same amount of fluoride leakage as that attained when it is not used, due to the longer heating times involved. Therefore it would appear that little would be gained by using it. Also, because at this stage the actual time required for heating had not yet been determined it was considered more important to determine this first. Then from fluoride leakage tests at the actual time a decision on whether the airway would be an advantage could be made and hence whether further development of the heat exchanger is necessary.

2-4.3 The Determination of the Time Required for the Heating Stage

In order to determine the time required for heating the water film to within 2 or 3 °C of the gas stream temperature, a series of Chromel/Alumel thermocouples were attached to the apparatus (Fig. 2-4.3a). This allowed the water film temperature to be continuously monitored, with time, against the gas stream temperature and hence the heating time was determined from the time required for the voltage to reach zero. This method, in comparison with the initial method (section 2-4.2), eliminated errors associated with heat losses from the sample cylinder and also reduced the errors associated with the unsteady conditions encountered at the fertilizer works.

Four thermocouples were used. One measured the water film temperature in the sample cylinder, one measured the gas stream temperature and two measured the atmospheric temperature outside the duct. The first thermocouple above, rotated with the cylinder, and so required slip rings. The incorporation of the two atmospheric thermocouples avoided creating an unknown thermocouple at the brass connectors for the slip rings and were arranged so that their voltages cancelled to zero. They also allowed the maximum voltage to be transferred through the slip rings as the water film temperature approached that of the gas stream (Fig. 2-4.3a), important because of the appreciable noise generated at the slip rings. Both these thermocouples were covered with insulation tape to make them less sensitive to temperature fluctuations caused, for example, by sudden wind gusts.

The thermocouple measuring the water film temperature was supported on a hinged bracket on the sample plug so that when the filter was closed (heating stage) the bracket lay on the inner surface of the sample cylinder with the thermocouple in the water measuring the temperature at that point (Fig. 2-4.3b, diagram 1). The centrifugal forces exerted on the bracket held the thermocouple in position. The hinged arrangement allowed the thermocouple to be lifted out of the rotating sample cylinder

when the filter was opened and locked in the stationary position and hence did not disturb the water film while fluoride absorption took place (Fig. 2-4.3b, diagram 2). In this position the bracket rested on the lip of the sample cylinder.

The thermocouple measuring the gas stream temperature was supported on a stationary copper tube with the thermocouple being as close as possible to the position of the thermocouple in the rotating sample cylinder. This was to avoid any temperature differences that may exist at different positions in the gas stream. The thermocouple was isolated from the copper tube in order to avoid erroneous temperature readings caused by the copper tube being cooler than the actual gas stream temperature (especially in the initial stages). The thermocouple was also insulated, using insulation tape, in order to reduce disturbances caused by minor rapid temperature fluctuations. These fluctuations were produced from small operating condition adjustments at the fertilizer works and from gas stream contaminants of varying temperature, such as entrained sludge, contacting the thermocouple.

All thermocouple wires were held in position on the apparatus with "Araldite" glue. Enough length of wire was allowed around the sample plug so that it could be fitted and removed without breaking any wires. A Phillips digital multimeter, accurate to ± 0.05 mV, was used to measure the voltage. The time was measured using a stopwatch, accuracy ± 0.2 s.

Several problems were encountered by using slip rings to transfer the millivolt signals to the voltmeter. Copper brushes on brass slip rings were used. One of the problems was that of making continuous contact between the brushes and the slip rings. This was enhanced by vibration of the apparatus due to a slight out-of-balance. However it was found that, by increasing the compressive force of the brushes on the slip rings, using small springs, continuous contact was possible. Another problem was the random voltage "noise" observed after approximately 2 minutes of continuous operation. This problem was overcome by spraying the brushes with "CRC" before each run. Water was also tried, however it was found less satisfactory as the brushes required

spraying after 4 or 5 minutes continuous running. Nagib et al (31) in a similar experimental set-up, where slip rings were used to transfer millivolt signals from a hot-thermister, found that spraying the brushes with water once every few hours continuous operation suppressed the noise to less than 1% of the signal. The slip ring rotation speed in their experiments varied from 0.07 to 110 rpm, which may account for the water being less satisfactory on the mass transfer apparatus (rotation speed ~1000 rpm). Also the increased force of the brushes on the slip rings may account for this.

In all heating time determinations the apparatus was loaded with water (10 cm^3) and placed vertically into the gas stream duct. The timing commenced as soon as the apparatus was seated in position and the voltage was recorded every 15 seconds until it had stabilised at zero. The gas stream temperatures were also recorded, approximately every minute, during each run using an alcohol-in-glass thermometer (accuracy $\pm 0.1 \text{ }^\circ\text{C}$). Before each run the apparatus was thoroughly washed with water, allowed to cool to ambient temperature and the brushes sprayed lightly with "CRC".

The voltages recorded from each run, once converted to degrees celsius, allowed a plot of the gas-water film temperature difference ($T_g - T_w$) versus time (t) to be constructed. The collective results for a series of runs where the airway through the apparatus was blocked off, is shown in Fig. 2-4.3c. A line of best fit has been drawn through the data. The gas temperature recorded for each run is the arithmetic mean value for all the measurements made during that run, with the error recorded being one standard deviation from the mean.

As can be seen, from Fig. 2-4.3c, the temperature of the water film approaches that of the gas asymptotically with the increase in water film temperature with time following the expected exponential curve. This can be seen more clearly in Fig. 2-4.3d where a plot of $\log_{10}(T_g - T_w)$ versus time is shown. A straight line was able to be drawn through the points having an equation, determined from least squares analysis, of:

$$\ln(T_g - T_w) = -0.46(t) + 4.5 \quad \text{correlation coefficient} = 98\%$$

where T_g, T_w = gas and water temperatures respectively /°C
 t = time /min

From these plots a suitable preheat time for absorption experiments can be chosen. Since a minimum heating time is required in order to keep the fluoride leakage to a minimum and to keep the sampling time required for the absorption to a minimum, thus reducing possible errors in the mass transfer coefficient caused by varying conditions at the fertilizer works, a time of 8 minutes was considered suitable. This allowed the water film to reach a temperature within 2 to 3 °C that of the gas, for gas temperatures less than 99 °C (Fig. 2-4.3d). This heating time, however, was less than the 14 minutes predicted from the heat transfer calculations (appendix 2).

To determine whether the fluoride leakage obtained after 8 minutes heating time was suitable for use as a background concentration in the absorption measurements, a series of repeated fluoride leakage measurements were made, without blowing air through the airway, by the method outlined in section 2-1.2. The concentration of the gas before and after each fluoride leakage measurement was also determined, using the method outlined in section 2-3.2. The results of these tests are shown in Table 2-4.3a.

The first point to notice from these results is that the gas concentrations did not remain constant throughout the sampling, but showed a general increase as the sampling proceeded. This increase is believed to be due to the total manufacturing/scrubbing system at the works coming to steady state after start-up (all sampling was unavoidably in this initial period). The variations from this trend are probably due to changes in manufacturing operating conditions. (The factors which affect the fluoride concentrations in the gas stream have been discussed in sections 1-2 and 1-4). Because of the changing gas concentrations the arithmetic mean of the concentrations measured before and after each fluoride leakage measurement are used to represent the conditions in the gas stream during the

leakage measurement. This creates an error ranging from approximately 6 to 9% for the representative gas concentrations, assuming a 3% error in each gas concentration measured (section 2-3.2).

The second point to notice is that the fluoride leakage concentrations were not constant throughout the sampling, as expected from the varying gas concentrations. However, they were low compared to those obtained initially when the apparatus was tested, considering the longer heating time and higher gas concentrations involved (section 2-4.1). The leakage was however significant and could result in an error as great as 20% in the mass transfer coefficient if it is not included in the calculations (this is assuming it to be the only error in the calculation, appendix 3). Therefore to determine the mass transfer coefficient accurately the fluoride leakage must be known accurately at the gas concentration encountered in the absorption experiment or be negligible. It is assumed that the only error in the fluoride leakage concentration is that occurring in the fluoride analysis i.e. a maximum of $\pm 2\%$ (section 2-3.1).

By plotting the fluoride leakage against the gas concentration (Fig. 2-4.3e) it is found that a linear relationship exists between the two. From least squares analysis, where the point (0,0) is used in the analysis, the linear equation is:

$$c_o = 233 \times 10^{-3} (c_g) + 26$$

where c_o = fluoride leakage concentration /ppm F

c_g = gas concentration /mg F m^{-3} dry air @ 0 °C

This equation has a correlation coefficient of 98% which indicates that the fluoride leakages obtained were consistent (at least for the day over which these results were collected). It was therefore considered that the fluoride leakages could be accurately obtained for each days sampling and hence could be used with confidence as a background concentration in the

absorption experiments required to determine the mass transfer coefficient. For this reason it was decided not necessary either to improve the heat exchanger or to use the airway to reduce the leakage any further (sections 2-4.1 and 2-4.2).

The linear relationships between the fluoride leakage and the gas concentration found was the first indication that the mass transfer coefficient was constant throughout the absorption (assumption 2, section 2-2) at these concentrations since:

$$k_g = \frac{(c_t - c_o) \cdot V}{A \cdot t \cdot c_{gs}} \quad (\text{equation 2, section 2-2})$$

where $c_t - c_o$ = fluoride leakage concentration = c_o
 c_{gs} = gas concentration leaked into the sample
cylinder = $c_{g,o}$
 V, A, t = constants
 k_g = mass transfer coefficient

Hence

$$c_o \propto c_{g,o}$$

$$= \frac{k_g \cdot A \cdot t \cdot c_{g,o}}{V}$$

Therefore for a linear relationship, k_g must be constant.

The value of the gas concentration leaked into the sample cylinder ($c_{g,o}$) is a function of the gas stream concentration (c_g) i.e. $c_{g,o} \propto c_g$. However, this function was dependent on how well sealed the sample cylinder was. Therefore if any changes in the operation of the seal occurred from day to day then one could expect a change in the proportionality constant between $c_{g,o}$ and c_g , and hence the slope of the fluoride leakage versus gas concentration plot. The sealing of the sample cylinder is dependent on the operation of the apparatus, for example the balance. If the balance deteriorates, then the sealing of the sample cylinder will also deteriorate due to the increased vibration causing the cover plate to "bounce" off and on the sample cylinder. However, the significance of the balance on the fluoride leakage is not known. (This is discussed in section 2-6).

Table 2-4.1a

Fluoride Absorption (Leakage) During the Heating Stage

(Average values only of repeated tests given)

Day	Time in Gas Stream min	Gas Temp. °C	Fluoride Concentration ppm F	Comments
1	0.5		4000	original sample
	2.5	81	24000	cylinder
	2(0.5)*		23000	(Fig. 2-1b)
2	2.5	79	30000	o-ring
	2.5		7000	o-ring, pump blocked
3	2	75	4000	new sample cylinder
	3		6500	(Fig. 2-1c)
4	1	79	1300	same as day 3
	3	80	4125	
5	2	79	3300	airway blocked
	2		2300	airway open, not blowing
6	2	81	960	airway blocked
	2		660	airway open, not blowing
7	2	92	3360	airway blocked
	2	93	2160	open, blow $\sim 4.5 \text{ l min}^{-1}$
8	2.5	96	4800	airway blocked
	2.5	97	2800	open, blow $\sim 4.5 \text{ l min}^{-1}$ gas conc. = 4700 mg F m^{-3}
9	2.5	95	5000	airway blocked
	2.5		700	airway blocked, shielded
	2.5		130	blow $\sim 10 \text{ l min}^{-1}$, shielded gas conc. = 5400 mg F m^{-3}

Table 2-4.1a (continued)

Day	Time in Gas Stream min	Gas Temp. °C	Fluoride Concentration ppm F	Comments
10	3	85	440	airway open, not blowing pump shielded
	3	85	305	blow ~1 l min ⁻¹ shielded
	3	85	276	blow ~2 l min ⁻¹ shielded
	3	84	316	blow ~3 l min ⁻¹ shielded
	3	84	103	blow ~4 l min ⁻¹ shielded
	3	85	210	blow ~6 l min ⁻¹ shielded
	3	85	176	blow ~7.5 l min ⁻¹ shielded gas conc. = 6000 mg F m ⁻³

* Filter closed for 2 minutes and open for 0.5 minute

Fig. 2-4.1a

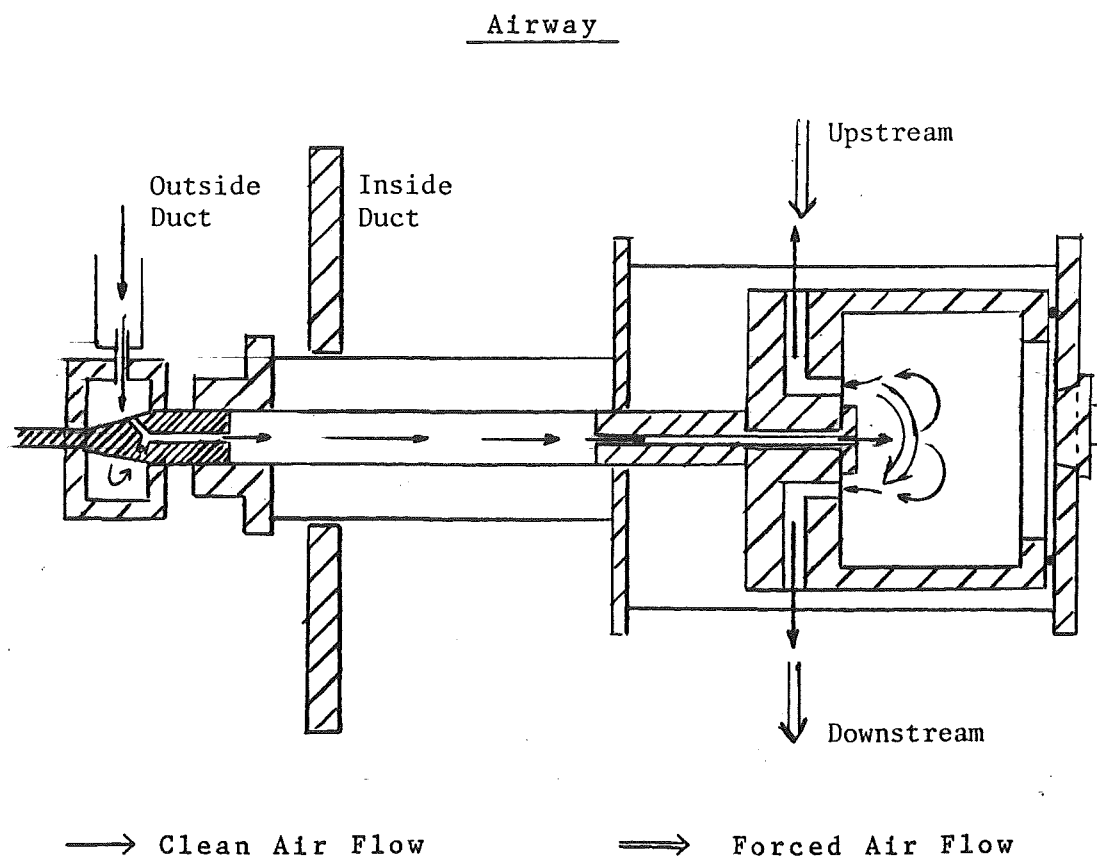


Fig. 2-4.1b

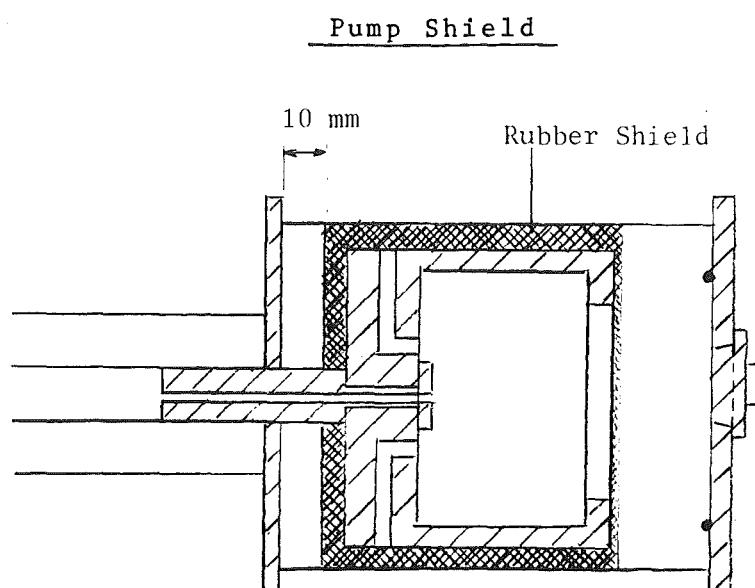


Table 2-4.2a

Heat Exchanger Effects on Heating Time

Gas ⁺ Temperature °C	Heating Time min	Hot * Airflow l min ⁻¹	Water Temperature °C	Method Used
Part A				
91	2	9	52	
91	3	0	66	U-Tube
90	3	9	57	Heat
90	4	0	70	Exchanger
90	4	9	63	
Part B				
94	2	9	50	Sample
94	< 2	0	> 52	Plug
94	3	9	61	Heat
95	3	0	68	Exchanger

⁺ Gas temperatures recorded once during each sampling.

Fig. 2-4.2a

Heat Exchanger

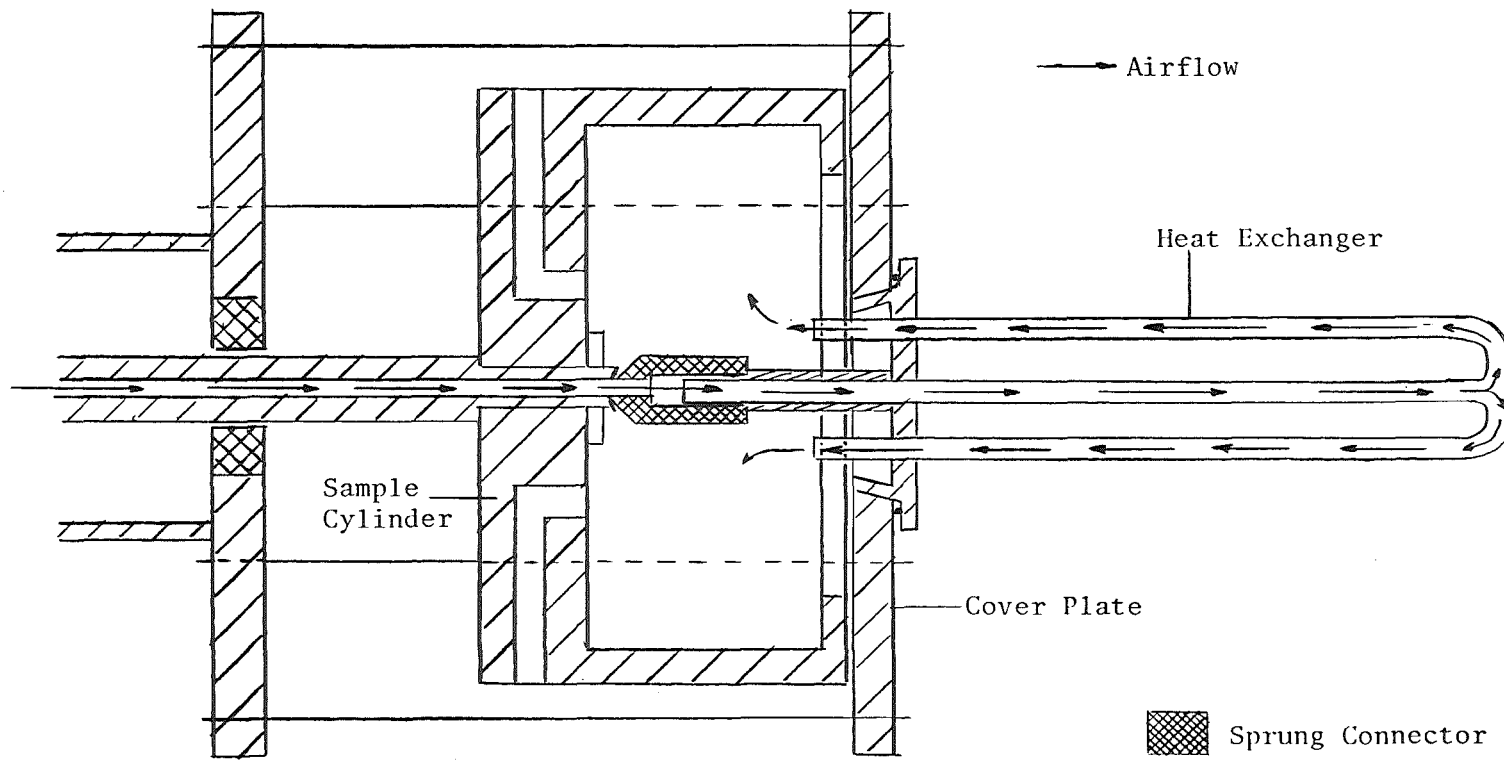


Fig. 2-4.3a Cromel/Alumel Thermocouples Attached to the Apparatus

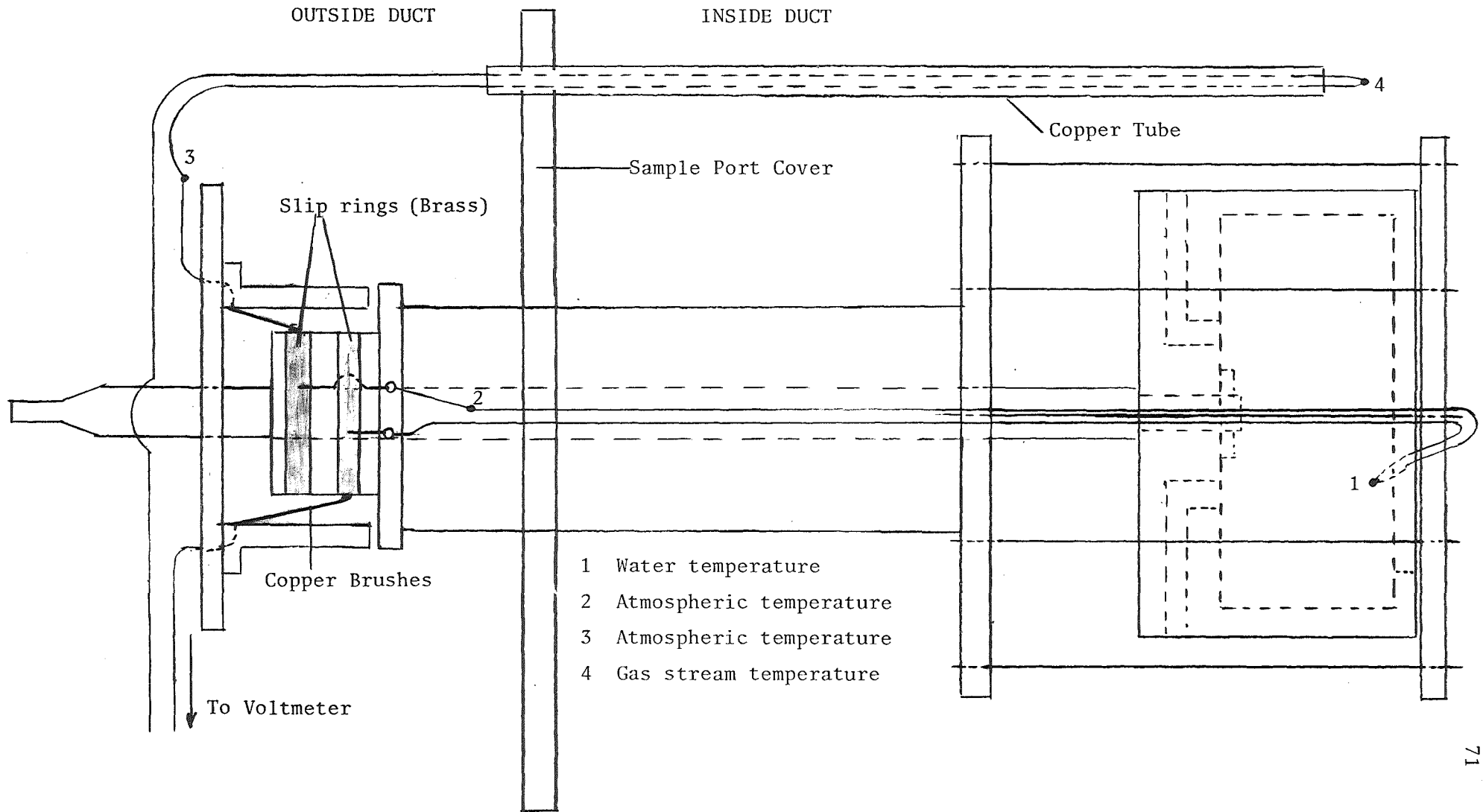


Fig. 2-4.3b

Hinged Thermocouple Bracket

Diagram 1 (Filter Shut)

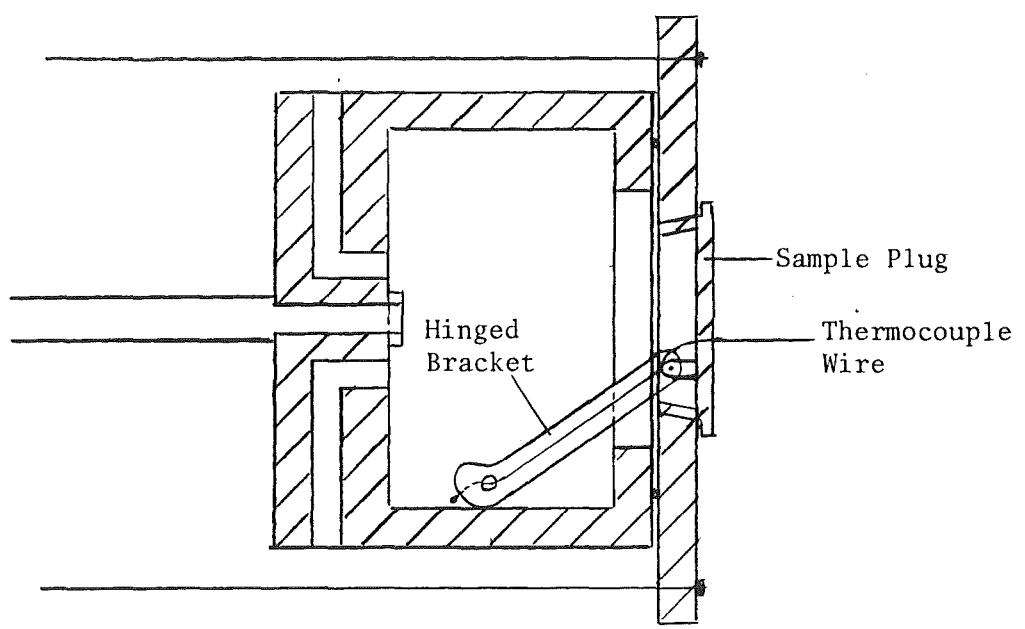


Diagram 2 (Filter Open)

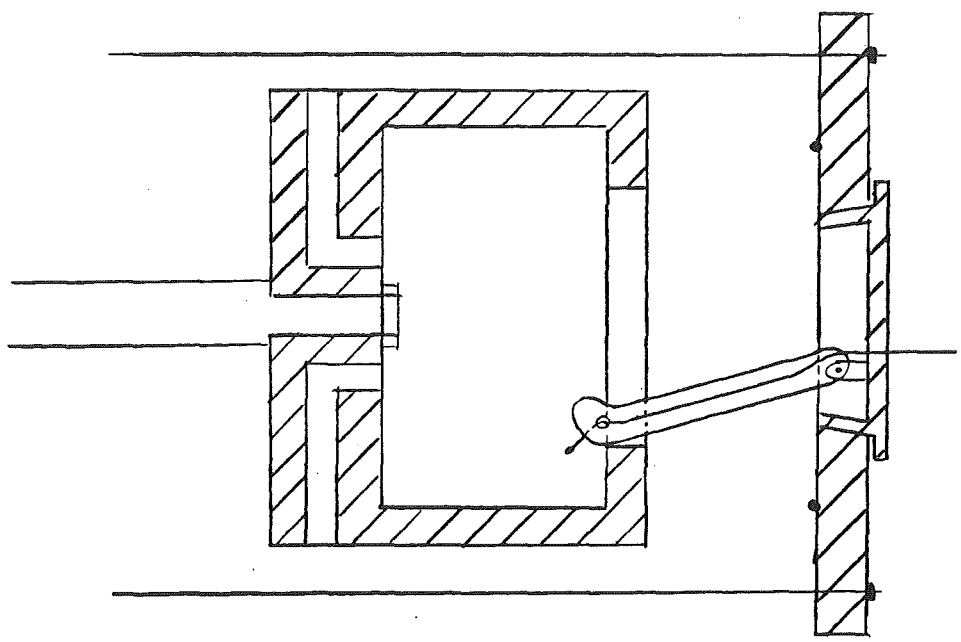


Fig. 2-4.3c

Gas Temperature - Water Film Temperature ($T_g - T_w$) versus Time (t)

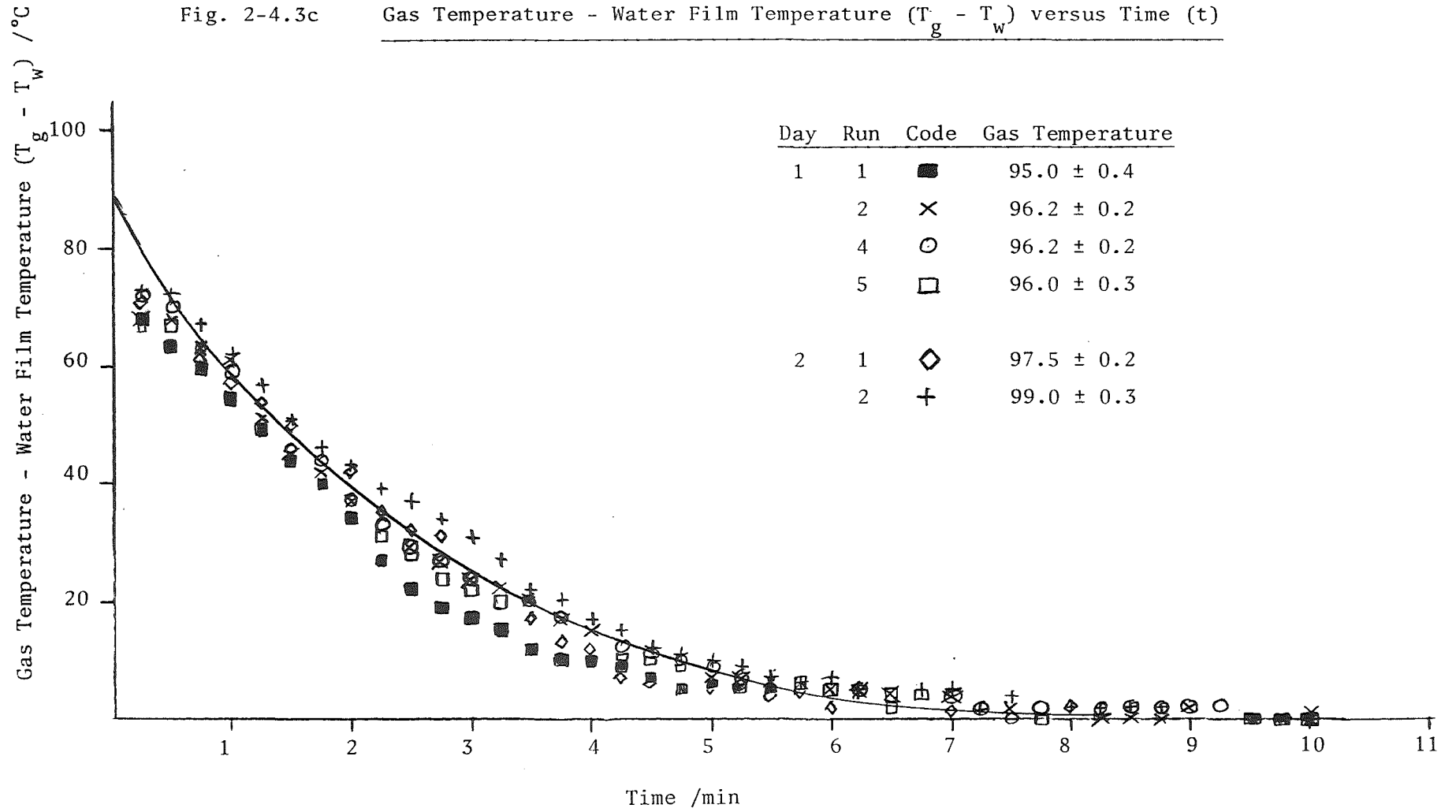


Fig. 2-4.3d

$T_g - T_w$ versus Time (t)

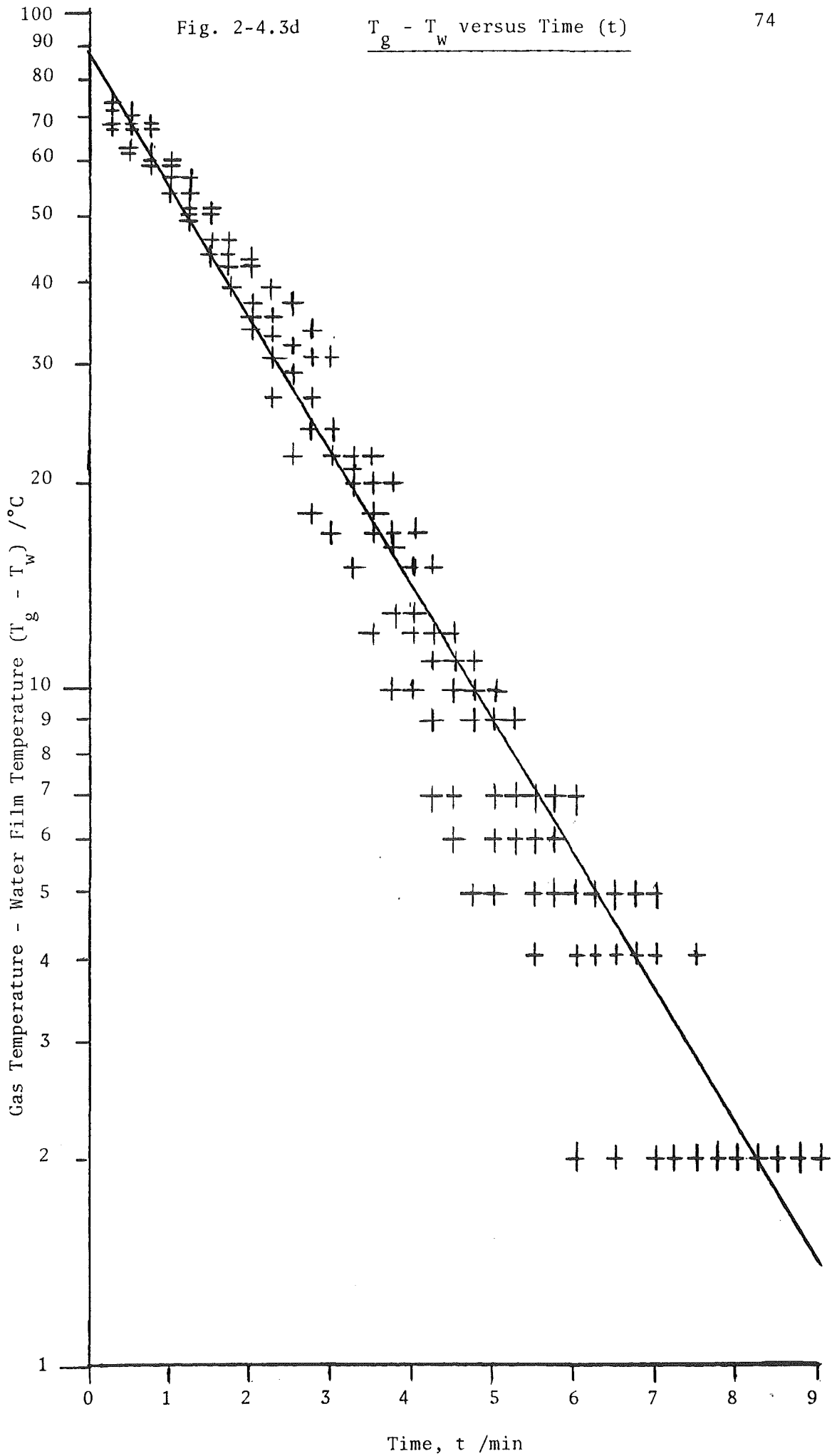


Table 2-4.3a

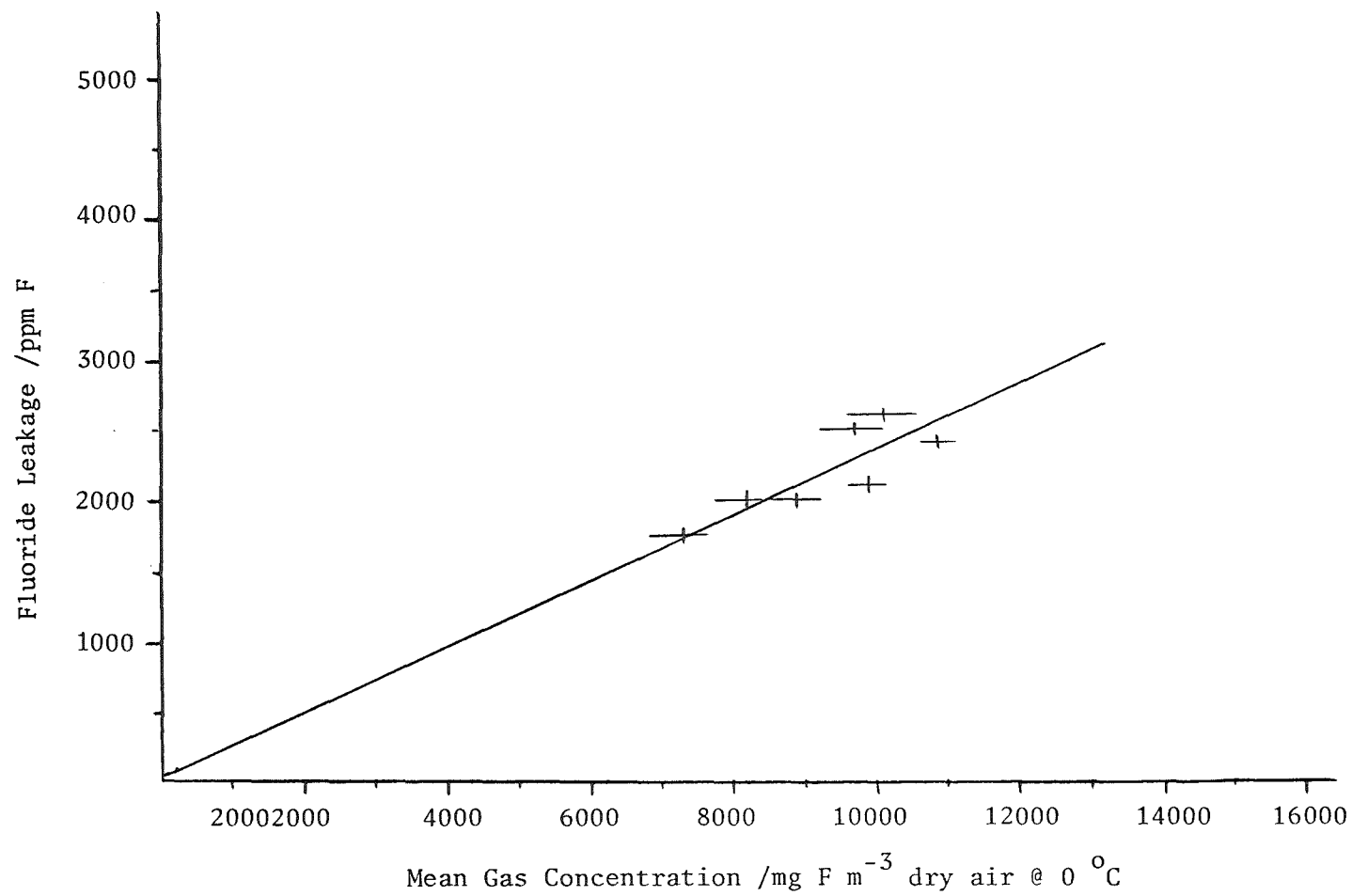
Fluoride Absorbed due to Leakage for Eight Minutes Heating Time
(without using the airway)

Gas Concentration (measured) mg F m ⁻³ @ 0 °C	Mean Gas * Concentration (calculated) mg F m ⁻³ @ 0 °C	Fluoride Leakage (Background Concentration) ppm F
6795	7259	1750
7723	8184	2000
8645	8937	2000
9228	9669	2500
10110	9863	2100
9615	10123	2600
10630	10914	2400
11197		

* Mean gas concentration calculated from the measured gas concentrations before and after each fluoride leakage concentration.

Fig. 2-4.3e

Fluoride Leakage versus Mean Gas Concentration



Section 2-5

Experimental Procedure Required for the Mass Transfer
Coefficient Determination

To measure the mass transfer coefficient for the "fluoride" absorption in water, using the apparatus, it is necessary to know; (1) the volume of water used, hence allowing the determination of the liquid-gas interfacial area; (2) the absorption time; (3) the fluoride concentrations of the gas stream and of the water before and after each absorption time, and also; (4) the gas temperature (section 2-2).

The volume of water used and the absorption times could both be measured accurately, for each sampling, using a syringe (accuracy $\pm 0.1 \text{ cm}^3$) and stopwatch (accuracy $\pm 0.2 \text{ s}$) respectively. However, because of the unsteady conditions encountered at the fertilizer works, it was necessary to measure the gas concentration and temperature regularly throughout the sampling. It was also necessary to determine the background concentration (fluoride leakage) regularly, as this was also known to vary with the gas concentrations (section 2-4.3) and it had to be determined whether any changes in the operation of the apparatus from day to day, had a significant effect on the fluoride leakage. Therefore, the following experimental procedure was adopted for the mass transfer coefficient determination.

- (1) Gas concentration: measured isokinetically by the procedure outlined in section 2-3.2.
- (2) Background concentration: measured using the mass transfer apparatus as described in section 2-1.2. An 8 minute heating time was always used.
- (3) Absorption concentration: measured using the mass transfer apparatus as described in section 2-1.2. Absorption times of 0.5 to 10 minutes were used.

This sequence (i.e. steps 1 to 3) were repeated for each days

sampling, finishing for the day with a gas concentration measurement. This allowed the calculation of a mean gas concentration to represent the conditions in the gas stream during the background and absorption measurements.

During each step of the procedure the gas temperature was recorded, approximately every minute using an alcohol-in-glass thermometer (accuracy ± 0.1 °C). This allowed the mean gas temperature to be calculated for the background and absorption measurements. The thermometer was removed from the gas stream between each step, for cleaning in order to reduce etching of the glass by the "fluorides".

Each absorption time was repeated at least twice, usually three times, to check on the consistency of the mass transfer coefficient calculated.

No sampling was conducted in the first hour of manufacture after start up due to the very unstable conditions. High scrubber liquor recycle rates were used during this first hour to allow the system to warm up quickly.

All equipment in contact with the fluoride solutions were washed thoroughly with deionized water and wiped dry with a clean dry tissue (where possible) after each measurement. The mass transfer apparatus was cooled quickly between each measurement by spraying with cold water.

Section 2-6

Results and Discussion

The results obtained from the experimentation are shown in Table 2-6a, where all gas concentrations have been expressed in units of mg F m^{-3} dry air @ 0 °C, and all aqueous fluoride concentrations as obtained from background and absorption measurements have been expressed in units of mass (ppm). The gas temperatures are the arithmetic mean of the temperatures taken during the sampling of the concentrations shown, with the "error" being one standard deviation from the mean. Any samples that were taken during a noticeable manufacturing problem or apparatus operation problem have been discarded along with other data obtained from that series. For example, when a manufacturing problem arose while taking a gas concentration measurement the the absorption and background concentration measurements preceeding it were also discarded and another gas concentration was measured once the process settled down again. The main manufacturing problems encountered were stops in production or stops in scrubber liquor recycle, both being easily detected by a sudden drop in gas temperature. A variety of apparatus operation problems were encountered.

The gas concentration variation for each day's sampling is found (Table 2-6a) to follow the same trend as that found in section 2-4.3. That is, a general increase in gas concentration occurs with time. This was attributed to the manufacturing/scrubbing process approaching steady state after start-up and the variations from this general trend were attributed to small undetectable changes in the manufacturing operating conditions. The general increase in gas temperature during each day's sampling (Table 2-6a) is also evidence for this.

The background concentrations (fluoride leakages) obtained appear at first sight to follow no particular trend (Table 2-6a). However, after plotting the background concentration against the arithmetic mean gas concentration $[(c_{g,1} + c_{g,2})/2]$ for each day's results it is found that the linear relationship shown in

section 2-4.3 does exist for these results (Fig. 2-6a). The linear equations for each day's results, as determined from least squares analysis, using the point (0,0) in the analysis, are shown in Table 2-6b (the equations for days 1 and 6 were not determined as only one background concentration was measured for each of these days due to manufacturing and sampling problems). Most of the equations determined have correlation coefficients above 96% indicating that the rate of fluoride leakage into the sample cylinder remains approximately constant for each day. However, on days 3 and 11 poorer correlations, 89 and 87% respectively, and higher background concentrations were obtained. On these days some operating problems were encountered with the apparatus.

On day 3, early on in the sampling, the threaded joint holding the filter support plate on to the "Tufnol" shaft gave way. However, by winding PVC tape around the thread the filter could be held tightly on the shaft and sampling could continue but, because of the difficulty in determining, on site, whether the filter was properly aligned, the balance of the apparatus had deteriorated. This deterioration in balance probably reduced the effectiveness of the seal between the cover plate and the sample cylinder (section 2-4.3) and hence allowed more fluoride to leak into the sample cylinder thus allowing the higher background concentrations (Fig. 2-6a). The poor correlation obtained is probably due to attempts made to improve the balance before some background measurements and hence changing the effectiveness of the sealing of the sample cylinder. These results, however, were not discarded as it is assumed that the balance of the apparatus remained the same for the two consecutive background and absorption measurements and therefore the rate of fluoride leakage will be the same for both.

In between days 3 and 4 the filter support plate was glued and pinned in position and the filter realigned. The heat exchanger (section 2-4.2) was also removed, since it was no longer required, and hence the balance of the apparatus had improved considerably for the rest of the sampling, as indicated by the reduction of fluoride leakage to approximately one half for the following days (excluding day 11). The high background

concentrations on days 1 and 2 are also probably due to the presence of the heat exchanger as any small knock created problems with the balance. The results obtained in section 2-4.3 (Fig. 2-4.3c) where the heat exchanger was also in position show a similar amount of fluoride leakage as that obtained for days 1 and 2.

The poor correlation and high background concentrations obtained on day 11 can also be attributed to a malfunction in the operation of the apparatus. This time the top bearing (Fig. 2-6b) on the filter mechanism overheated, caused by a washer being "stuck" against the bearing. The washer was used to reduce the wear on the bearing by rotating with the rotating spring while the filter was locked in the stationary position. However, because the washer had "stuck", the heat generated by the rotating spring on the washer caused the bearing to expand and jam against the stainless steel shaft. Some of the bearing had also melted onto the shaft, making opening and closing of the filter mechanism difficult during the sampling and hence the tension created by the spring between the cover plate and the sample cylinder was probably reduced, also reducing the effectiveness of the seal. These results were also not discarded as it was again assumed that the apparatus would operate similarly for the two consecutive background and absorption measurements.

In between days 11 and 12 the shaft was cleaned down and the washer freed and some high temperature stopcock grease used to lubricate between the bearing and the washer. No further problems of overheating were encountered.

For the days 4, 5, 7, 8, 9, 10 and 12 the background concentrations obtained are, as mentioned, approximately one half that obtained for the other days as no major problems were encountered for these days. However, as can be seen (Fig. 2-6a) the variation in background concentration with gas concentration does not lie on the same line. This is believed to be due to small variations from day to day in the balance of the apparatus caused from dismantling and assembling the apparatus for repairs or cleaning. Although a reasonably good correlation is achieved

for these days the background concentration used in calculating the mass transfer coefficient will be taken as that measured before the absorption concentration used in the calculation, rather than using the equation from the plot. This is done to avoid possible errors created by small changes in the operation of the apparatus for each day.

The gas concentration used to represent the condition in the gas stream during the background and absorption measurements has been taken as being the arithmetic mean of the two gas concentrations ($c_{g,1}$ and $c_{g,2}$) bracketing both measurements (Table 2-6a). This is considered to be the largest source of error in calculating the mass transfer coefficient as the discrepancy between the two may be as high as 15% depending on the time elapsed between taking each sample and the operation of the manufacturing process. However, in most cases the discrepancy is approximately 5%.

The mass transfer coefficients calculated from these results are shown in Table 2-6c where $k_{g,1}$ and $k_{g,2}$ are the coefficients obtained from equations (1) and (2) section 2-2 respectively, where both values have been calculated at the mean gas temperature (T_g). The error associated with each value is in the range 25 to 35% for $k_{g,1}$ and 15 to 25% for $k_{g,2}$. A sample calculation and error analysis is given in appendix 4.

The first point to notice from these results (Table 2-6c) is that the value of k_g calculated for each day and hence differing absorption times, is relatively constant (i.e. within experimental error), indicating that the assumptions made in the calculations (section 2-2) do hold. Also comparison between the values of $k_{g,1}$ and $k_{g,2}$ indicate that the significance of the (non zero) interface vapour pressures on the mass transfer rate was negligible. The interface vapour pressures, as expected, become more significant at the longer absorption times (higher liquor concentrations) and at the higher temperatures. However, the largest discrepancy obtained between the two values is only 14% which is considered insignificant compared to the errors involved in each method. It must also be remembered that the vapour pressure data used in the calculations was that for

solutions free of dissolved phosphate rock (section 2-2.1). Therefore the vapour pressures used may be higher than actually present due to the possibility of entrained phosphate rock being dissolved in the solutions, which is known to lower the vapour pressures (3). This would mean that the actual mass transfer coefficient may be inbetween the value of $k_{g,1}$ and $k_{g,2}$ calculated.

The second point to notice from these results (Table 2-6c) is that the mass transfer coefficients obtained are not only constant for each day but also remain relatively constant for all the days 1 to 7 (i.e. $k_{g,1} = 103 \pm 19 \text{ m h}^{-1}$ and $k_{g,2} = 96 \pm 17 \text{ m h}^{-1}$). However, on day 8 a reduction of approximately 46% occurs in the value which then remains relatively constant for the rest of the days (i.e. $k_{g,1} = 55 \pm 13 \text{ m h}^{-1}$ and $k_{g,2} = 53 \pm 13 \text{ m h}^{-1}$). The consistency of the results can be seen in Fig. 2-6c where a plot of $(c_t - c_o)/c_g$ versus time (t) is shown for the days 1 to 7 and the days 8 to 12. From least squares analysis the equations of the lines (both have correlation coefficients greater than 97%) are:

For days 1 to 7

$$(c_t - c_o)/c_{gs} = 840(t) + 33$$

For days 8 to 12

$$(c_t - c_o)/c_{gs} = 411(t) + 125$$

where c_t , c_o , c_{gs} = absorption, background and gas
concentrations respectively /mg F m⁻³
t = time /min

The slopes of these lines equal $k_{g,2} \cdot A/V$ (equation (2), section 2-2).

The reasons for the reduction in the mass transfer coefficient observed at day 8 is not altogether obvious. However, for such a reduction to occur there must be either a change in the manufacturing process producing different conditions in the gas stream or a change in the operation of the

sampling apparatus or both.

A search through the company records for these days revealed that no noticeable changes in the manufacturing process occurred that would consistently affect the mass transfer rate. There were no consistent changes in the rock blend or rock fineness or scrubber liquor recycle rate used and hence no consistent changes in the amount of rock dust carryover or fluoride concentration in the gas stream. The mean temperature for the gas for days 1 to 7 is 97 ± 2 °C and for days 8 to 12 is 96 ± 2 °C. This difference is not considered significant to account for such a large variation in k_g , especially when the temperature range for both days 1 to 7 and days 8 to 12 is the same (i.e. 92 to 99 °C).

A change in the operation of the mass transfer apparatus however did occur. In between days 7 and 8 the stainless steel filter mesh on the apparatus was replaced, because of its badly corroded state, especially on the side facing directly into the gas stream. The mesh had also collapsed under the rubber shield, where cleaning was difficult, and was catching on the exterior of the sample cylinder, making opening and closing of the filter mechanism difficult. A filter mesh as close as possible to the original was used to replace it (mesh size 11.5 per cm, original 11 per cm). Also, because the new mesh was of slightly thicker gauge than the original a small shaving had to be taken off the exterior of the sample cylinder (~0.8 mm) to allow enough clearance between the new filter and the sample cylinder for opening and closing of the filter mechanism. This slight narrowing of the sample cylinder wall is believed to have a negligible effect on the time required for heating the water film because (as found in section 2-4.3) the water film was being heated from both the inside and outside of the sample cylinder. Even if the sample cylinder was perfectly sealed in the heating stage and the transfer of heat was only through the sample cylinder wall then a thinner wall by approximately 0.8 mm would decrease the time of heating by approximately one minute. Assuming the thinner wall allowed the water film temperature to come closer to equilibrium with the gas stream temperature, than on days 1 to 7 a slightly higher temperature difference between

the gas stream and water film would exist. However, this temperature difference would only be, at the most, 2 to 3 °C (Fig. 2-4.3b, section 2-4.3) and hence any thermal diffusion occurring would be negligible and could not explain the difference in mass transfer coefficients obtained.

If the original filter, because of its badly corroded state, allowed contamination of the sample by entrained particles (as found in the sludge in the bottom of the duct, section 1-3), then the value of k_g calculated on days 1 to 7 would include fluoride from captured particles. Also, if the particles entrained had not reached the gas stream velocity at the gas sampling point, then the measured gas fluoride concentration (including particulates) would have been less than the actual concentration (including particulates) in the gas stream. (This can be significant for larger sized particles i.e. greater than 50 micrometres). This would give an erroneous value for k_g initially (days 1 to 7).

By using a fibreglass filter on the gas sampling probe (Fig. 2-6d) an estimate of the particulate concentration in the gas stream was obtained (Table 2-6d). It appears that approximately 25% of the fluorides are in particulate form capable of being removed by a fibreglass filter. (The consistency of this value from day to day is unknown, but, because the operating conditions at the fertilizer works remained relatively constant over all the days of sampling the particulate concentration should not vary greatly). It was also found that by using a stainless steel filter mesh on the gas sampling probe inlet, identical to that used on the mass transfer apparatus, that very little of the particulates present were removed from the gas stream (less than 1%, Table 2-6d). This would suggest that the filter mechanism on the mass transfer apparatus, for days 8 and onwards, was capable of removing only those particulates of size greater than that being collected during isokinetic sampling of the gas stream. (Particulates were observed on the filter mesh of the apparatus after the absorption measurements). Hence the value of k_g for the first group of days was high due to these larger fluoride particles passing through the corroded filter and into the sample cylinder. An alternative

possibility is that the new filter mesh on the mass transfer apparatus was removing more than that found with the filter mesh on the sampling probe due to particulate build-up on the apparatus' filter reducing the size of the particulates able to pass through. However, in order for this to happen the filter must block very quickly when in the stationary position (when spinning it was essentially free from build-up), otherwise one would expect the mass transfer coefficient to decrease with increasing absorption time. This is not the case and hence it is believed that the capture of particles by the mesh does not affect significantly further capture.

It would appear therefore that the later value for k_g is more correct since the gas (with particulates) entering the sample cylinder is that measured in the gas stream and the earlier higher value for k_g is probably due to larger particles, undetected by sampling with the sampling probe in the gas stream, entering the sample cylinder and being absorbed in the water. That is, for the temperature range encountered (92 to 99 °C) and for a gas stream containing approximately 25% particulate fluorides, the absolute value for the mass transfer coefficient, k_g in our spinning sampler is $55 \pm 13 \text{ m h}^{-1}$.

It was suggested (section 1-3) that although the absorption is gas phase controlled initially for dry silicon tetrafluoride in water, the absorption would become liquid phase controlling as the silica produced in the absorption formed a solid film at the liquid-gas interface. The results of this work indicate, by the constancy in the mass transfer coefficient obtained over all the absorption times, that the resistance remains gas phase controlling. This is probably due to the silica produced not being able to form a solid film at the surface due to the centrifuging effect of the rotational motion of the apparatus. Hence fresh liquid surfaces are continuously created throughout the absorption.

Comparison of the results of this work with that by Whynes (41) and Koval et al (22) is difficult due to the different flow characteristics of the gas and liquid phases and the presence of particulates. However, from a study on the sublimation of

naphthalene using the same mass transfer apparatus (43) a theoretical gas phase mass transfer coefficient for silicon tetrafluoride absorption was determined and hence from a comparison of this value with that determined experimentally an indication of the particulate component in the absorption can be obtained. It was first found that for naphthalene the value of k_g was proportional to the gas stream velocity (in this case the angular velocity at the interface) raised to the power of 0.8, as also found by Gilliland and Sherwood (15) for the vapourisation of liquids at 20 °C. A different proportionality constant was found in this study compared with that of Gilliland and Sherwood, because of the different flow system. However, from simple ratios for the mass transfer apparatus a theoretical value of k_g for silicon tetrafluoride absorption was determined from that measured for naphthalene (appendix 5).

$$k_{g,a}/k_{g,b} = (Re_a/Re_b)^{0.8} \cdot (Sc_a/Sc_b)^{0.44} \cdot (D'_a/D'_b)$$

where k_g = gas phase mass transfer coefficient

Re = gas Reynolds number

Sc = Schmidt number

D' = diffusivity in air

subscripts: a = silicon tetrafluoride ; b = naphthalene

The theoretical gas phase mass transfer coefficient for silicon tetrafluoride absorption was then $k_g(\text{theor}) = 66 \pm 10 \text{ m h}^{-1}$, allowing for a 15% error in the value for naphthalene. By comparing the experimental and theoretical (gaseous) mass transfer fluxes it can be seen that the presence of particulate fluorides increases the rate by approximately 11%. This is calculated from the fact that 25% of the fluorides present in the gas stream are in particulate form and therefore the gaseous mass transfer flux is given by:

$$M(\text{gas}) = k_g(\text{theor})[1 - 0.25] \cdot c_g = 0.75 \cdot k_g(\text{theor}) \cdot c_g$$

where $M(\text{gas})$ = gaseous mass transfer flux

$k_g(\text{theor})$ = gaseous mass transfer coefficient

c_g = total fluoride (gaseous + particulate)
concentration in gas stream

Thus the mass transfer flux due to particulates is:

$$M(\text{part}) = [k_g(\text{expt}) - 0.75.k_g(\text{theor})].c_g$$

where $M(\text{part})$ = particulate mass transfer flux

$k_g(\text{expt})$ = experimental mass transfer coefficient

From this difference, and by considering the drift flux of particulates to the water film surface under centrifugal action in the apparatus, an estimate of the size of the particulates present in the gas stream can be determined. It was found (appendix 6, part 1) that:

$$D_p^2 \cdot \rho_p = 7.3 \times 10^{-9} \text{ kg m}^{-1}$$

where D_p = particle diameter

ρ_p = particle density

Therefore by assuming ρ_p is between 1000 and 2000 kg m^{-3} :

$$D_p = 1.9 \text{ to } 2.7 \text{ micrometres}$$

Further verification of this value for $D_p^2 \cdot \rho_p$ could be obtained by doing runs with the mass transfer apparatus at different rotation speeds. The influence of rotation speed on the absorption is to increase both the gaseous and particulate components with the particulate component increasing at a greater rate than the gaseous. At the rotation speed used in this work the particulate component is 10% of the total fluoride collected, however from a calculation based on appendix 6, part 1, it is expected that this will increase to 20% at twice the rotational speed (appendix 7).

By using the value of $D_p^2 \cdot \rho_p$ given above it is possible to determine the collection efficiency of these particulates by water droplets and hence sprays (38). For example, it was found (appendix 6, part 2) that a water drop (0.5 mm diameter) falling at its terminal velocity (2.2 m s^{-1}) is capable of capturing only approximately 2% of the particulates in its path and that in order to remove 99% of the particulates present in a gas stream

(using water sprays producing 0.5 mm diameter drops, falling at their terminal velocity in a horizontal duct, see appendix 6, part 2) approximately 16.5 litres of water is required per cubic metre of gas. Therefore the liquid to gas ratio required to reduce the fluoride levels expelled to the atmosphere down to an acceptable level in a single stage scrubber is not only limited to that required to absorb the gaseous fluorides but also, more importantly, to that required to capture the particulate fluorides. Since such a high percentage of the fluorides in the gas stream are in particulate form (~25%) then this is the limiting condition for the liquid to gas ratio (appendix 6, part 2) and hence the concentration of scrubber liquor possible. e.g. for a gas concentration of $10000 \text{ mg F m}^{-3}$ entering a scrubber, a maximum liquor concentration without recirculation is only approximately 0.06% F (w/w), using the conditions in the above example appendix 6, part 3. This would suggest a large water recirculation flow around one stage in a multistage scrubber, at least, is required to remove the particulates (a much larger flow than is required for gas absorption). It would probably be best to arrange this for the first stage, which appears to be what is done at the fertilizer works at Hornby (of the 12 compartments in the scrubber at Hornby, the liquid to gas ratio per compartment for the first 8 is approximately twice that used in the last compartment - this may not be optimal, and a higher ratio may be beneficial).

The gas phase (without particulates) mass transfer coefficient for silicon tetrafluoride absorption into water droplets (4.1 mm diameter at room temperature) was found by Koval et al (22) to be 253 m h^{-1} . This value checks well with theoretical calculations (appendix 8, part 1). Hence using the theory it is possible to calculate gas phase coefficients at various gas temperatures and drop sizes for silicon tetrafluoride absorption. By knowing this value along with the value of $D_p^2 \cdot Q_p$ a more accurate measure of the total (gaseous + particulate) mass transfer to water droplets should be possible.

The collection of particulates is expected to be poor in low velocity single stage operations where the residence time is short. In scrubbing systems where the residence time is long or

where continued scrubbing occurs, causing a significant reduction in gas temperature, there is also the influence of the condensing water vapour on the collection efficiency of particulates. If the gas is cooled by the introduction of water drops causing water vapour to condense on the particulates then the increase in size of the particulates will improve the collection efficiency of the drops and hence the gaseous component may become the limiting factor in the absorption. However, for this to happen the heat transfer to the gas by conduction from the water drops must be greater than the heat transfer by condensation to the water drops. This is found, by considering a single drop in a saturated gas (appendix 9), not to be the case. It appears that the heat transfer by condensation is approximately 50 times greater than the heat transfer by conduction. Therefore it is expected that the collection of the particulate fluoride component will remain the limiting component in a multistage scrubber. The flux of water vapour to the water drops due to condensation, however, will aid in the capture and absorption of both the fluoride components. This effect is known as diffusiphoresis.

The scrubber at the Hornby fertilizer works operated satisfactorily using approximately 4.8 litres of absorption liquor per cubic metre of gas, of which 4.6 litres is recirculated scrubber liquor, which is considerably less than the 16.5 litres predicted by the calculations in appendix 6. This can probably be explained by the effect of diffusiphoresis and the higher relative velocities between the phases in the works scrubber than accounted for in the above calculation.

Table 2-6a

Raw Data for the Mass Transfer Coefficient Determination

Symbols used below are defined at end of table

Day	t min	T _g °C	c _{g,1} mg F m ⁻³	c _o ppm F	c _t ppm F	c _{g,2} mg F m ⁻³
1	1	96.7 ± 0.8	23522	1080	7750	25245
2	1	94.5 ± 0.9	14045	4700	11268	15838
	1	95.6 ± 0.7	16900	5100	12259	18001
	1	95.6 ± 0.8	18001	5300	-----	19397
3	1	92 ± 1	8168	2500	65000	8955
	1	92.2 ± 0.8	5749	1800	7875	7145
	2	93.5 ± 0.4	7145	2650	9750	8005
	2	95 ± 1	8005	2500	9750	9224
	3	95.5 ± 0.3	9224	1882	13750	7850
	3	96.3 ± 0.8	7850	1565	15500	8650
4	2	97.3 ± 0.6	8996	1940	15000	12888
	2	98.2 ± 0.4	12888	2500	15750	14881
	2	98.4 ± 0.5	14881	2300	17125	16343
	4	98.9 ± 0.8	16343	2100	32000	17132
	4	98.8 ± 0.8	17132	3350	27000	19284
	4	98.8 ± 0.8	19284	2750	35000	19012
5	5	96.6 ± 0.8	13307	2100	35500	15900
	5	97.1 ± 0.4	15900	2600	42000	16997
	5	97.3 ± 0.4	16997	2900	46000	20888
	6	97.5 ± 0.5	20888	2800	60000	20400
	6	97.7 ± 0.3	20400	2850	6100	21133
6	1.5	98.4 ± 0.7	16075	3100	13865	17738
7	1.5	97.6 ± 0.8	12743	2000	12000	16235
	1.5	97.9 ± 0.6	16235	2040	13250	15305
	1.5	98.4 ± 0.4	15305	2400	13500	15260
	0.5	97.9 ± 0.3	15260	2800	6690	16283
	0.5	97.6 ± 0.8	16283	3000	7700	17893
	0.5	97.1 ± 0.7	17893	2600	5775	14123
	3	96.3 ± 0.5	14123	2400	22400	13429
	3	96.5 ± 0.4	13429	2150	23650	14762

Table 2-6a (continued)

Day	t min	T _g °C	c _{g,1} mg F m ⁻³	c _o ppm F	c _t ppm F	c _{g,2} mg F m ⁻³
8	1	98.0 ± 0.7	17040	1840	4500	18093
	0.5	98.4 ± 0.4	21894	2100	4000	21110
	0.5	98.7 ± 0.8	15559	1920	4250	20744
	2.5	99.0 ± 0.4	20744	1940	14750	20923
	2.5	98.2 ± 0.6	20923	2300	14750	16045
9	2.5	97.3 ± 0.8	22557	3650	20950	21611
	2.5	98.7 ± 0.5	21611	2600	20288	25324
	2.5	99.3 ± 0.4	25324	3650	22125	26845
10	2	95.2 ± 0.4	10972	1320	7200	13352
	1	95.2 ± 0.4	14528	1750	----	15168
	1	95.4 ± 0.6	15168	2400	7850	17073
	1	95.5 ± 0.5	17073	1900	9440	16299
11	3	92.6 ± 0.7	8987	2170	11844	10618
	3	92.9 ± 0.4	10618	4130	15998	13217
	3	92.9 ± 0.7	13217	4670	17750	13050
	5	93.7 ± 0.5	13050	2530	20675	14843
	5	94.5 ± 0.6	14843	3740	23500	14947
	5	94.5 ± 0.4	18493	4700	21090	16482
12	7	93.9 ± 0.7	12239	1590	26250	13463
	7	95 ± 1	13463	2070	29700	12942
	10	95.7 ± 0.9	12942	2380	47250	18475
	10	95.8 ± 0.6	18475	3560	55500	24627

t = absorption time

T_g = gas stream temperature

c_{g,1} & c_{g,2} = gas concentrations respectively before and after
background and absorption measurements

c_o & c_t = background and absorption concentrations
respectively

Fig. 2-6a

Background Concentration (c_o) versus Mean Gas Concentration (c_g)

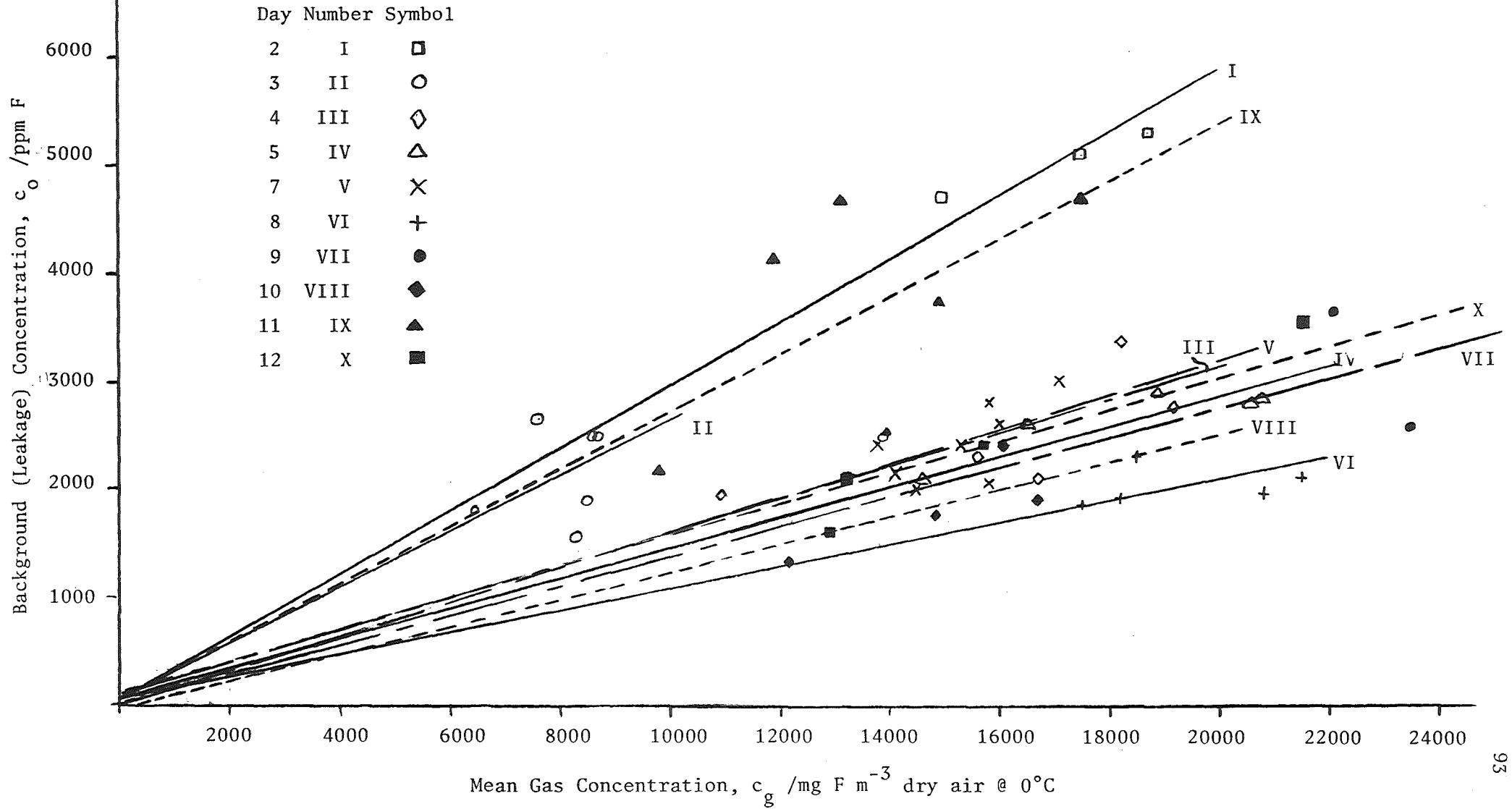


Table 2-6b

Linear Equations Representing the Relationship Between the
Background Concentration (c_o) and the Gas Concentration (c_g)

Day	Number *	Equation **	Correlation
2	I	$c_o = 291 \times 10^{-3} \cdot c_g + 57$	100%
3	II	$c_o = 260 \times 10^{-3} \cdot c_g + 62$	89%
4	III	$c_o = 151 \times 10^{-3} \cdot c_g + 98$	96%
5	IV	$c_o = 141 \times 10^{-3} \cdot c_g + 54$	99%
7	V	$c_o = 161 \times 10^{-3} \cdot c_g - 32$	96%
8	VI	$c_o = 101 \times 10^{-3} \cdot c_g + 51$	97%
9	VII	$c_o = 137 \times 10^{-3} \cdot c_g + 29$	96%
10	VIII	$c_o = 127 \times 10^{-3} \cdot c_g - 45$	97%
11	IX	$c_o = 264 \times 10^{-3} \cdot c_g + 69$	87%
12	X	$c_o = 162 \times 10^{-3} \cdot c_g - 130$	99%

* Number refers to the line in Fig. 2-6a

** Equation refers to that determined from least squares analysis. The point zero background concentration at zero gas concentration was used in the analysis.

Fig. 2-6b

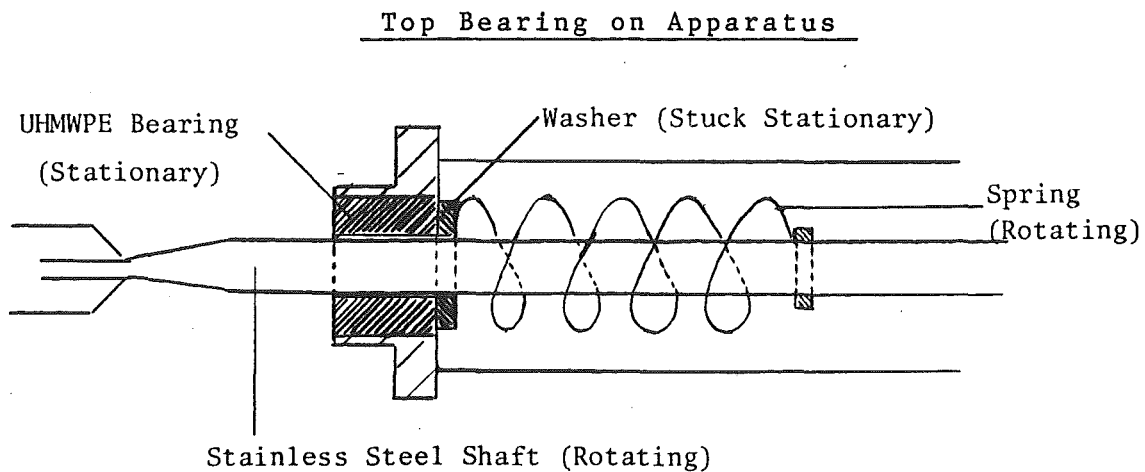


Table 2-6c

Mass Transfer Coefficients

Day	Absorption Time t, min	Gas Temperature T _g , °C	k _{g,1} * m h ⁻¹	k _{g,2} + m h ⁻¹
1	1	96.7 ± 0.8	50.4	49.8
2	1	94.5 ± 0.9	92.3	89.5
	1	95.6 ± 0.7	84.7	82.0
	1	95.6 ± 0.8	----	----
3	1	92 ± 1	98.4	96.2
	2	92.2 ± 0.8	100.7	97.6
	2	93.5 ± 0.4	101.5	97.2
	2	95 ± 1	88.4	84.6
	3	95.5 ± 0.3	102.7	96.4
	3	96.3 ± 0.8	139.2	127.4
4	2	97.3 ± 0.6	150.8	139.6
	2	98.2 ± 0.4	108.3	101.4
	2	98.4 ± 0.5	107.4	100.7
	4	98.9 ± 0.8	104.1	92.8
	4	98.8 ± 0.8	66.9	61.6
	4	98.8 ± 0.8	95.4	85.8
5	5	96.6 ± 0.4	105.8	95.1
	5	97.1 ± 0.4	114.9	101.5
	5	97.3 ± 0.4	106.6	94.7
	6	97.5 ± 0.5	112.0	96.7
	6	97.7 ± 0.3	114.5	98.1
6	1.5	98.4 ± 0.7	88.7	84.5
7	1.5	97.6 ± 0.8	100.5	96.2
	1.5	97.9 ± 0.6	105.0	100.3
	1.5	98.4 ± 0.4	109.2	103.5
	0.5	97.9 ± 0.3	109.1	106.0
	0.5	97.6 ± 0.8	127.5	123.8
	0.5	97.1 ± 0.7	80.5	78.9
	3	96.3 ± 0.5	110.2	102.6
	3	96.5 ± 0.4	118.8	110.0
Mean		97 ± 2	103 ± 19	96 ± 17

Table 2-6c (continued)

Day	Absorption Time t, min	Gas Temperature $T_g, ^\circ\text{C}$	$k_{g,1}^*$ m h^{-1}	$k_{g,2}^+$ m h^{-1}
8	0.5	98.0 ± 0.7	57.3	56.5
	0.5	98.4 ± 0.4	30.7	30.3
	0.5	98.7 ± 0.8	47.2	46.5
	2.5	99.0 ± 0.4	45.9	44.2
	2.5	98.2 ± 0.6	51.1	49.1
9	2.5	97.3 ± 0.8	61.3	58.7
	2.5	98.7 ± 0.5	58.9	56.3
	2.5	99.3 ± 0.4	54.9	52.3
10	2	95.2 ± 0.4	43.7	42.8
	1	95.2 ± 0.4	----	----
	1	95.4 ± 0.6	65.3	64.0
	1	95.5 ± 0.5	95.3	93.2
11	3	92.6 ± 0.7	63.2	61.3
	3	92.9 ± 0.4	64.4	62.1
	3	92.9 ± 0.7	64.5	62.1
	5	93.7 ± 0.5	48.3	46.5
	5	94.5 ± 0.6	50.0	47.7
	5	94.5 ± 0.4	33.2	32.2
12	7	93.9 ± 0.7	52.1	49.9
	7	95 ± 1	59.0	55.0
	10	95.7 ± 0.9	57.9	52.2
	10	95.8 ± 0.6	46.6	42.0
Mean		96 ± 2	55 ± 13	53 ± 13

* $k_{g,1}$ = mass transfer coefficient calculated by taking into account the (non zero) interface vapour pressures (equation (1), section 2-2).

+ $k_{g,2}$ = mass transfer coefficient calculated assuming the vapour pressures are negligible (equation (2), section 2-2).

Fig. 2-6c

$$\frac{c_t - c_o}{c_{g,s}} \text{ versus Time}$$

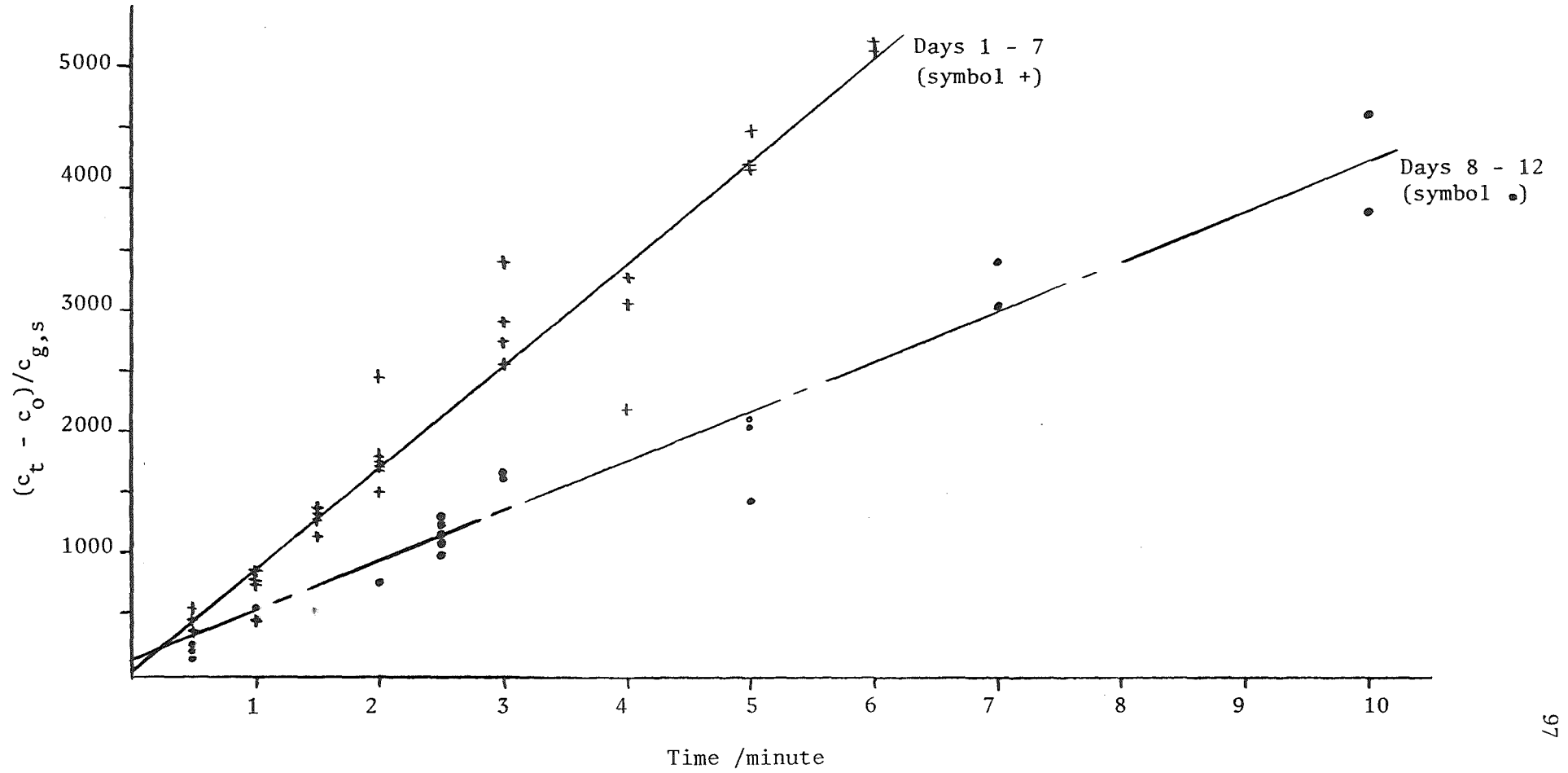


Table 2-6d

Particulate Fluoride Determination

Run	Method *	Gas stream Temperature °C	Fluoride Concentration mg F m ⁻³ @ 0 °C
1	A	93.2 ± 0.4	7864
2	B	93.6 ± 0.3	7761
3	C	93.6 ± 0.5	7500
4	A	94.1 ± 0.1	9772
5	B	93.9 ± 0.1	10022
6	C	94.3 ± 0.5	8082
7	A	94.6 ± 0.2	10688
8	B	95.2 ± 0.2	10301
9	C	94.9 ± 0.4	8812
10	A	95.8 ± 0.3	11852

Mean concentrations: Gas stream (runs 1, 4, 7) = 9441 mg F m⁻³
 Gas stream (runs 4, 7, 10) = 10771 mg F m⁻³
 Filter mesh (runs 2, 5, 8) = 9361 mg F m⁻³
 Fibre Filter (runs 3, 6, 9) = 8131 mg F m⁻³

Percentage filtered: Filter mesh = (1 - 9361/9441).100
 = 0.9%

Fibre Filter = (1 - 8131/10771).100
 = 25%

* Method

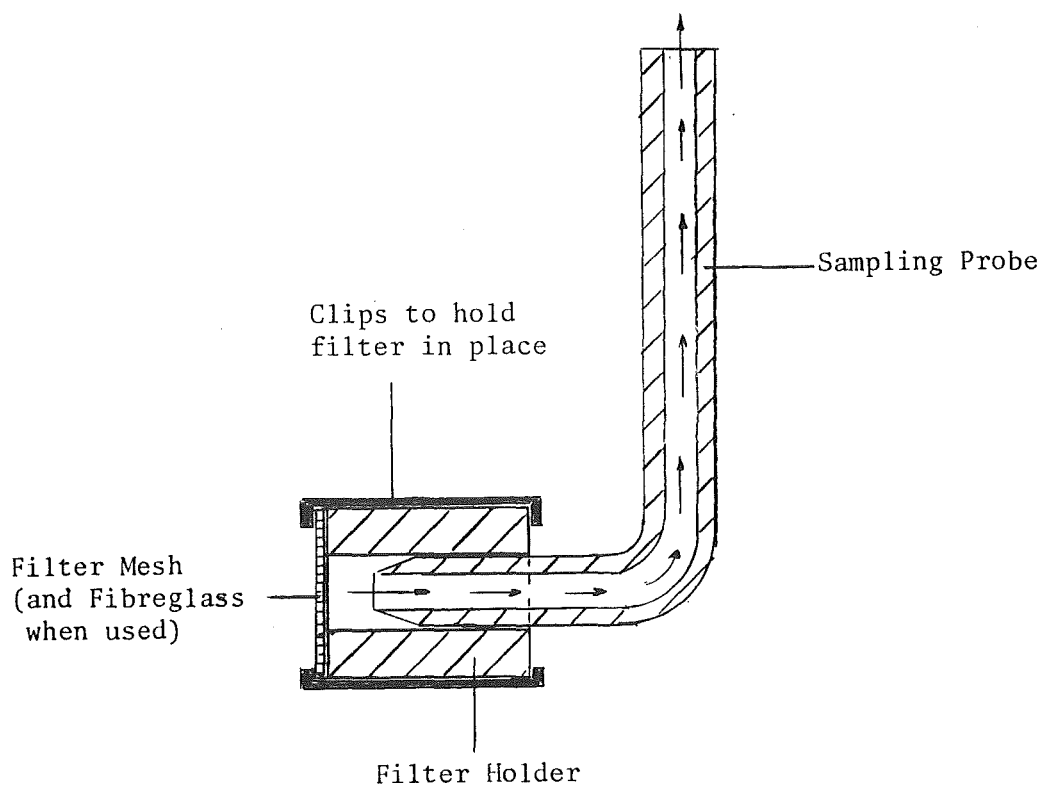
- A : Isokinetic sampling of the gas stream as determined by the method section 2-3.2
- B : Isokinetic sampling of the gas stream with a stainless steel filter mesh on the sampling probe inlet (Fig. 2-6d). Filter mesh is identical to that used on the mass transfer apparatus. Two minutes were allowed for the filter, facing downstream, to heat up.
- C : The same as method B except with a fibreglass filter

over the stainless steel filter mesh.

All sampling was done with the probe at the same depth and position in the gas stream duct as that of the sample cylinder of the mass transfer apparatus.

Fig. 2-6d

Filter Holder



Section 2-7

Conclusions

- (1) The gas stream fluorides are not purely in the form of silicon tetrafluoride gas; particulate fluorides are also present.
- (2) The gas phase resistance is controlling in the absorption with the significance of the (non zero) interface vapour pressures being negligible.
- (3) The presence of particulates increases the mass transfer rate in the mass transfer apparatus. This increase is believed to be related to the rotational speed of the sample cylinder.
- (4) The results obtained with the apparatus allow the determination of the size of the particulates present ($D_p^2 \cdot Q_p = 7.3 \times 10^{-9} \text{ kg m}^{-1}$) and hence allow the calculation of the increased mass transfer caused by particulates in spray droplets.
- (5) A suitable fluoride scrubber for the fertilizer industry must be capable of absorbing the gaseous component as well as capturing the particulates. The particulate component may often be the controlling factor.

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Appendix 1

Error in Gas Concentration

$$c_g = \frac{c_{aq} \cdot V_{w,T} \cdot \rho_{w,T} \cdot (T + 273)}{273 \cdot V_{g,T}} \quad (\text{section 2-3.2})$$

Errors in each value are:

1. Fluoride concentration (c_{aq}) :

Error is ~2% maximum. (section 2-3.1)

2. Fluoride solution volume ($V_{w,T}$) :

Approximately 600 cm³ of solution was measured each time using a measuring cylinder (accuracy ± 2 cm³). Therefore the error in measuring is ~0.33%. A dilution of 5/100 was required to bring the solution to the desired concentration range, i.e. 10-100 ppm F. Therefore the additional error is ~0.42%. Hence the total volume error is ~0.75%.

3. Gas volume withdrawn ($V_{g,T}$) :

Approximately 20.0 litres of gas was withdrawn, accuracy of the gas meter is ± 0.05 litres. Therefore the error is ~0.25%.

4. Gas temperature at gas meter (T):

The gas temperature is usually 15 °C, accuracy of the temperature gauge is ± 0.5 °C. Therefore the error is ~0.17%.

5. Density of solution water ($\rho_{w,T}$) :

Error is taken as being negligible (34).

Therefore the maximum error in the gas concentration (c_g) is ~3%.

Appendix 2

Estimation of the Time Required to Heat the Water Film to Within
Two Degrees Celsius of the Gas Stream Temperature

We will assume that the time required to heat the water film is the same as the time required to heat the plastic sample cylinder wall (thickness = 6.5 mm) and the sample cylinder is only heated by the gas stream flowing over the cylinder.

$$\text{Rate of heat transfer, } Q = h_o \cdot A_o \cdot (T_g - T_s) = (dT_s/dt) \cdot C_p \cdot m_s \quad (1)$$

where h_o = convective heat transfer coefficient
(gas to sample cylinder surface)

A_o = surface area through which heat
transfer is based on

T_g = gas temperature

T_s = sample cylinder temperature

t = time

C_p = specific heat capacity of plastic

m_s = mass of sample cylinder wall

Integrating equation (1), assuming h_o , A_o , C_p and m_s are constant, such that;

$$\text{At } t = 0 ; T_s = T_{s,i}$$

$$\text{and at } t = t ; T_s = T_{s,f}$$

then:

$$\ln[(T_g - T_{s,i}) / (T_g - T_{s,f})] = (h_o \cdot A_o / C_p \cdot m_s) \cdot t \quad (2)$$

The maximum heating time is at the maximum gas temperature (T_g) and at the minimum initial sample cylinder temperature ($T_{s,i}$).

Therefore let;

$$T_g = 99 \text{ } ^\circ\text{C}$$

$$T_{s,i} = 10 \text{ } ^\circ\text{C}$$

We want the final sample cylinder temperature ($T_{s,f}$) within 2 $^\circ\text{C}$ that of the gas temperature.

Therefore;

$$T_{s,f} = 97 \text{ } ^\circ\text{C}$$

Now the dimensions of the sample cylinder are: (Fig. 2-1c)

$$\begin{aligned} \text{outside diameter } (D_o) &= 73 \times 10^{-3} \text{ m} \\ \text{inside diameter } (D_i) &= 60 \times 10^{-3} \text{ m} \\ \text{width } (W) &= 30 \times 10^{-3} \text{ m} \end{aligned}$$

$$\begin{aligned} \text{Therefore: } A_o &= 6.88 \times 10^{-3} \text{ m}^{-2} \\ \text{and } m_s &= (\pi/4) \cdot W \cdot (D_o - D_i)^2 \cdot \rho_s \\ &= (4.07 \times 10^{-5} \text{ m}^3)(950 \text{ kg m}^{-3}) \\ &= 3.87 \times 10^{-2} \text{ kg} \end{aligned}$$

The value of h_o can be calculated by the method given in M^cCabe and Smith (28), assuming the temperature of the outer surface of the wall to be the log mean temperature (T'_s) at the start of the sampling and at the end.

$$\begin{aligned} \text{i.e. } T'_s &= (99-10)/\ln(99/10) \\ &= 39 \text{ }^\circ\text{C} \end{aligned}$$

All physical properties of the gas are evaluated at T'_s . The gas is assumed to be dry air.

$$h_o \cdot D_o / k_o = \psi (u \cdot D_o / \nu) \quad (\text{M}^c\text{Cabe and Smith (28)})$$

The velocity of the gas stream, $u = 11 \text{ m s}^{-1}$ (ν = kinematic viscosity). Therefore:

$$u \cdot D_o / \nu = 51000$$

From the plot given in M^cCabe and Smith (28) this gives

$$\begin{aligned} h_o \cdot D_o / k_o &= 160 \\ \text{therefore } h_o &= 59 \text{ W m}^{-2} \text{ K}^{-1} \\ \text{and hence } 1/h_o \cdot A_o &= 2.46 \text{ K W}^{-1} \end{aligned}$$

Hence using equation (2) above the time required for heating the sample cylinder to within 2 $^\circ\text{C}$ that of the gas stream temperature is:

$$\begin{aligned} t &= (C_p \cdot m_s / h_o \cdot A_o) \cdot \ln[(T_g - T_{s,i}) / (T_g - T_{s,f})] \quad (\text{equation 2}) \\ &= (2302 \text{ J kg}^{-1} \text{ K}^{-1})(3.87 \times 10^{-2} \text{ kg}) / (2.46 \text{ K s J}^{-1}) \\ &\quad \times \ln\{(99 - 10) / (99 - 97)\} \\ &= \underline{14 \text{ minutes}} \end{aligned}$$

Therefore the approximate time required to heat the water film (considering the assumptions made) is 14 minutes.

Appendix 3

Error Incurred by Not Including the Fluoride Leakage as
a Background Concentration in the Mass Transfer
Coefficient Calculation

It will be assumed that the vapour pressures above the fluoride solutions are negligible. Therefore:

$$k_g = \frac{(c_t - c_o) \cdot V}{A \cdot t \cdot c_{gs}} \quad (\text{section 2-2.1})$$

Let the gas concentration, $c_{gs} = 10000 \text{ mg F m}^{-3}$ @ 96°C and the fluoride leakage after 8 minutes heating, $c_o = 2000 \text{ ppm F} \approx 2000 \times 10^3 \text{ mg F m}^{-3}$ (These values being the average values encountered at the fertilizer works).

The water volume, $V = 10 \times 10^{-6} \text{ m}^3$ and hence the water film surface area, $A = 5.3 \times 10^{-3} \text{ m}^2$.

The mass transfer coefficient given by Koval et al (22) will be assumed. i.e. $k_g = 253 \text{ m h}^{-1} = 0.07 \text{ m s}^{-1}$

The maximum error will be incurred for the minimum absorption time (t). Therefore, let $t = 30 \text{ s}$

Hence the fluoride liquor concentration obtained from the apparatus under the above conditions would be:

$$\begin{aligned} c_t &= c_o + (k_g \cdot A \cdot t \cdot c_{gs} / V) \\ &= 2000 \times 10^3 + [(0.07)(5.3 \times 10^{-3})(30)(10000) / (10 \times 10^{-6})] \\ &= 13174 \times 10^3 \text{ mg F m}^{-3} \end{aligned}$$

Now, by calculating the value of k_g , ignoring the fluoride leakage, and comparing with the value assumed above (253 m h^{-1}) an indication of the error involved is obtained.

i.e.

$$\begin{aligned} k_g &= \frac{c_t \cdot V}{A \cdot t \cdot c_{gs}} \\ &= (13174 \times 10^3)(10 \times 10^{-6}) / (5.3 \times 10^{-3})(30/3600)(10000) \\ &= 298 \text{ m h}^{-1} \end{aligned}$$

Therefore the error incurred in the value of k_g , for an

absorption time of 30 s (assuming no errors exist in the values of V, A, t, c_0 and c_{gs} used) is;

$$\begin{aligned}k_g &= (298 - 253)/253 \times 100 \\ &= 18\% \sim 20\%\end{aligned}$$

This error would decrease as the absorption time increased.

Appendix 4

Sample Calculation for the Mass Transfer Coefficient

From section 2-2, the value of the mass transfer coefficient can be calculated from either;

$$k_{g,1} = \frac{V}{A \cdot t \cdot m} \cdot \ln \frac{c_{gs} - m \cdot c_o}{c_{gs} - m \cdot c_t} \text{-----(1)}$$

or

$$k_{g,2} = \frac{(c_t - c_o) \cdot V}{A \cdot t \cdot c_{gs}} \text{-----(2)}$$

where k_g = mass transfer coefficient
 c_{gs} = gas concentration in sample cylinder
 c_o = background concentration
 c_t = absorption concentration
 m = slope of vapour pressure line = $f(T)$
 V = volume of absorption water
 t = absorption time
 A = liquid-gas interfacial area (equation (3), section 2-2)

For the gas temperatures encountered at the fertilizer works (i.e. 90 to 100 °C), the liquid-gas interfacial area for a $10.0 \pm 0.1 \text{ cm}^3$ sample measured at atmospheric temperature (15 to 25 °C) is taken as $(5.30 \pm 0.03) \times 10^{-3} \text{ m}^2$ in all the mass transfer coefficient calculations. The variation in area for the temperatures in the range 90 to 100 °C is insignificant compared to the calculated error and therefore is ignored.

The data day 3, run 1 (Table 2-6a, section 2-6) is used for the sample calculation.

Absorption time *	:	t	=	$60 \pm 2 \text{ s}$
Gas temperature	:	T_g	=	$92 \pm 1 \text{ }^\circ\text{C}$
Gas concentration (before)	:	$c_{g,1}$	=	$8168 \text{ mg F m}^{-3} @ 0 \text{ }^\circ\text{C}$
(after)	:	$c_{g,2}$	=	$8955 \text{ mg F m}^{-3} @ 0 \text{ }^\circ\text{C}$

Background concentration *	:	c_o	=	2500 ppm F
Absorption concentration	:	c_t	=	6500 ppm F
Atmospheric temperature	:	T	=	22 °C
Water volume @ $T = 22$ °C	:	V	=	$(10.0 \pm 0.1) \times 10^{-6} \text{ m}^3$
Liquid-gas interfacial area @ T_g :		A	=	$(5.30 \pm 0.03) \times 10^{-3} \text{ m}^2$

* values measured after the 8 minute temperature equilibration

The mean gas concentration (c_g) used to represent the conditions in the gas stream during the absorption and background measurements is:

$$c_g = [(c_{g,1} - c_{g,2})/2][273/(273 + T_g)] \\ = 6404 \pm 300 \text{ mg F m}^{-3}$$

The error associated with each absorption and background measurement is taken as being $\pm 2\%$. i.e. the maximum error associated with the fluoride analysis. Therefore:

$$c_t = 6500 \pm 130 \text{ ppm F } [\approx 6500 \times 10^3 \text{ mg F m}^{-3}] \\ c_o = 2500 \pm 50 \text{ ppm F } [\approx 2500 \times 10^3 \text{ mg F m}^{-3}]$$

The mean gas concentration in the sample cylinder during the absorption measurements (c_{gs}) is calculated using the equation:

$$c_{gs} = c_g - (c_t - c_o) \cdot V / 2 \cdot t \cdot Q \quad (\text{section 2-2}) \\ = 6404 - (4000 \times 10^3)(10 \times 10^{-6}) / 2 \cdot (60)(196 \times 10^{-6}) \\ = 4703 \pm 500 \text{ mg F m}^{-3}$$

The vapour pressures at the gas temperature are determined from equation (3), section 2-2.1.

i.e.

$$c_E = m \cdot c_1 \\ = \exp[130.7 \times 10^{-3}(T_g) - 15.5][273/(273 + T_g)] \cdot c_1$$

Therefore at 92 °C the value of m is:

$$m = 23.1 \times 10^{-3} \text{ kg(H}_2\text{O) m}^{-3}(\text{gas}).$$

An error of 5% is assumed in this value (section 2-2.1).

Therefore:

$$\begin{aligned} m &= (23 \pm 1) \times 10^{-3} \text{ kg(H}_2\text{O) m}^{-3}\text{(gas)} \\ &\approx (23 \pm 1) \times 10^{-6} \text{ m}^3\text{(H}_2\text{O) m}^{-3}\text{(gas)} \end{aligned}$$

Therefore the value of $k_{g,1}$ (equation 1) is:

$$\begin{aligned} k_{g,1} &= \frac{V}{A \cdot t \cdot m} \cdot \ln \frac{c_{gs} - m \cdot c_o}{c_{gs} - m \cdot c_t} \\ &= \frac{10 \times 10^{-6}}{(5.30 \times 10^{-3})(60)(23 \times 10^{-6})} \\ &\quad \times \ln \frac{4703 - (23 \times 10^{-6})(2500 \times 10^3)}{4703 - (23 \times 10^{-6})(6500 \times 10^3)} \\ &= 0.0273 \text{ m s}^{-1} \\ &= 98.4 \text{ m h}^{-1} \end{aligned}$$

To calculate the error in this value ($k_{g,1}$) the maximum value of $k_{g,1}$ is calculated. For $k_{g,1}$ to be a maximum:

Gas temperature	: T_g	= maximum = 93 °C
Gas concentration:	c_{gs}	= minimum = 4203 mg F m ⁻³
Volume	: V	= maximum = 10.1 × 10 ⁻⁶
Area	: A	= minimum = 5.27 × 10 ⁻³ m ²
Time	: t	= minimum = 58 s

The slope m at 93 °C (assuming a 5% error in the value) is:

$$m = (26 \pm 1) \times 10^{-6} \text{ m}^3\text{(H}_2\text{O) m}^{-3}\text{(gas)}$$

Therefore

$$\begin{aligned} m \cdot c_o &= \text{maximum} = (27 \times 10^{-6})(2550 \times 10^3) \text{ mg F m}^{-3} \\ m \cdot c_t &= \text{maximum} = (27 \times 10^{-6})(6630 \times 10^3) \text{ mg F m}^{-3} \end{aligned}$$

The value of m is a minimum in the portion $V/A \cdot t \cdot m$ (equation (1)) for $k_{g,1}$ to be a maximum. Hence $m = 25 \times 10^{-6} \text{ m}^3\text{(H}_2\text{O) m}^{-3}\text{(gas)}$.

Therefore

$$\begin{aligned} k_{g,1}(\text{max}) &= \frac{V}{A \cdot t \cdot m} \cdot \ln \frac{c_{gs} - m \cdot c_o}{c_{gs} - m \cdot c_t} \\ &= \frac{10.1 \times 10^{-6}}{(5.27 \times 10^{-3})(58)(25 \times 10^{-6})} \\ &\quad \times \ln \frac{4203 - (27 \times 10^{-6})(2550 \times 10^3)}{4203 - (27 \times 10^{-6})(6630 \times 10^3)} \\ &= 0.0357 \text{ m s}^{-1} \\ &= 128.5 \text{ m h}^{-1} \end{aligned}$$

Hence the maximum (but unlikely) error is:

$$\begin{aligned} (k_{g,1(\max)} - k_{g,1})/k_{g,1} \times 100 &= (128.5 - 98.4)/98.4 \times 100 \\ &= 30\% \end{aligned}$$

Therefore

$$\underline{k_{g,1} = 98 \pm 30 \text{ m h}^{-1}}$$

The error in the value of $k_{g,2}$ (equation 2) is:

$$\begin{aligned} k_{g,2} &= \frac{(c_t - c_o).V}{A.t.c_{gs}} \\ &= \frac{[(4000 \pm 180) \times 10^3][(10.0 \pm 0.1) \times 10^{-6}]}{[(5.30 \pm 0.03) \times 10^{-3}][60 \pm 2][4703 \pm 500]} \\ &= 0.0267 \text{ m s}^{-1} \quad (\pm 20.0\%) \\ &= \underline{96 \pm 19 \text{ m h}^{-1}} \end{aligned}$$

The error was calculated similarly for other runs and it was found to be in the range:

$$k_{g,1} = \pm 25-35\%$$

$$k_{g,2} = \pm 15-25\%$$

Note: This is extreme

Appendix 5

Determination of the Theoretical (Gaseous) Mass Transfer
Coefficient for Silicon Tetrafluoride Absorption

Results for the sublimation of naphthalene (43):

Rotation Speed /rpm	Mass Transfer Coefficient $k_g(\text{naph}) / \text{m h}^{-1}$
1030-1070	45.8
2250-2450	72.6
2300-2500	81.9

Need to show that these measurements do not contradict $k_g \propto v^{0.8}$

where k_g = mass transfer coefficient
 v = velocity relative to liquid-gas
 interface \propto rotation speed, n

If $k_g \propto v^{0.8}$, then

$$(k_{g,2}/k_{g,1}) = (n_2/n_1)^{0.8}$$

Thus

$$k_{g,2} = (n_2/n_1)^{0.8} \cdot k_{g,1}$$

Allowing for a 15% error in the values of k_g for naphthalene then:

$$k_{g,2} = (2350/1050)^{0.8} \cdot (45.8) = 87 \pm 13 \text{ m h}^{-1}$$

This agrees with the values given in the table above, within experimental error. Therefore, since $k_g \propto (\text{gas velocity})^{0.8}$ as found by Gilliland and Sherwood (15) then their relationship relating Sherwood number (Sh) to Reynolds (Re) and Schmidt (Sc) numbers can be used to determine a theoretical value of k_g for silicon tetrafluoride absorption.

i.e.

$$\text{Sh} \propto \text{Re}^{0.8} \cdot \text{Sc}^{0.44}$$

$$\Rightarrow k_g \propto \text{Re}^{0.8} \cdot \text{Sc}^{0.44} \cdot D'/L$$

where D' = diffusivity in air
 and L = characteristic length

$$\begin{aligned}
 \text{Thus } k_{g,a}/k_{g,b} &= (Re_a/Re_b)^{0.8} \cdot (Sc_a/Sc_b)^{0.44} \cdot D_a^-/D_b^- \\
 &= (\nu_b/\nu_a)^{0.8} \cdot (\nu_a \cdot D_b^-/D_a^- \cdot \nu_b)^{0.44} \cdot D_a^-/D_b^- \\
 &= (\nu_b/\nu_a)^{0.36} \cdot (D_a^-/D_b^-)^{0.56}
 \end{aligned}$$

where ν = kinematic viscosity

subscripts a = silicon tetrafluoride

b = naphthalene

$$\begin{aligned}
 \text{Now;} \quad k_{g,b} &= 46 \pm 7 \text{ m h}^{-1} (\pm 15\%) \text{ at low rotation speed} \\
 \nu_a &= 2.254 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} @ 96 \text{ }^\circ\text{C} \\
 \nu_b &= 1.469 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} @ 16 \text{ }^\circ\text{C} \\
 D_a^- &= 1.40 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} @ 96 \text{ }^\circ\text{C} \\
 D_b^- &= 5.59 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} @ 16 \text{ }^\circ\text{C}
 \end{aligned}$$

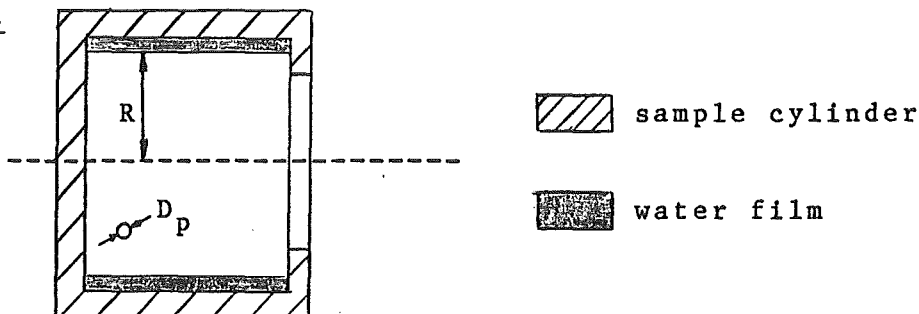
Therefore

$$\begin{aligned}
 k_{g,a} &= (\nu_b/\nu_a)^{0.36} \cdot (D_a^-/D_b^-)^{0.56} \cdot k_{g,b} \\
 &= (1.469 \times 10^{-5} / 2.254 \times 10^{-5})^{0.36} \\
 &\quad \times (1.40 \times 10^{-5} / 5.59 \times 10^{-6})^{0.56} \cdot (46 \pm 7) \\
 &= 66 \pm 10 \text{ m h}^{-1}
 \end{aligned}$$

i.e.

At low rotation speed of the mass transfer apparatus (as was used throughout this work) the theoretical (gaseous) mass transfer coefficient, $k_g(\text{theor}) = 66 \pm 10 \text{ m h}^{-1}$

Appendix 6

Mass Transfer due to Fluoride Particles in the Sample CylinderPart 1

Assume that the gas, and hence particulates, rotate with the water film at the film surface forming a boundary layer through which the particulates must pass. It is assumed that the concentration of the particulates at the boundary layer is that in the bulk gas.

Mass flux of particulates to the water film, $H = m_F \cdot N \cdot v_r$ ----(1)

where m_F = mass of fluoride per particle
 N = number concentration of particles
 v_r = radial drift velocity = $t_p \cdot a_r$
 a_r = acceleration of particles
 t_p = relaxation time of particles

$$a_r = \frac{(2 \cdot \pi \cdot n \cdot R)^2}{R} \quad n = \text{revolutions per second}$$

$$= 4 \cdot \pi^2 \cdot n^2 \cdot R \quad R = \text{radius of water film}$$

Assuming Stokes Law then:

$$t_p = \frac{D_p^2 \cdot \rho_p}{18 \cdot \mu} \quad D_p = \text{particle diameter}$$

$$\rho_p = \text{particle density}$$

$$\mu = \text{viscosity of carrier gas}$$

Therefore the mass flux of the particulates, H is:

$$H = \frac{m_F \cdot N \cdot D_p^2 \cdot \rho_p \cdot 4 \cdot \pi^2 \cdot n^2 \cdot R}{18 \cdot \mu}$$

$$= \frac{2 \cdot m_F \cdot N \cdot D_p^2 \cdot \rho_p \cdot \pi^2 \cdot n^2 \cdot R}{9 \cdot \mu} \quad \text{-----(2)}$$

Now, from comparison of gas sampling with and without a fibreglass filter;

$$m_F \cdot N = 0.25 \cdot c_g \quad c_g = \text{total fluoride concentration in the gas stream}$$

And;

$$\begin{aligned} \text{mass flux of} & \quad \text{mass flux of pure} & \quad \text{mass flux} \\ \text{particulates (H)} & = \text{gas and particulates} & \quad \text{of pure gas} \\ & = k_g(\text{expt}) \cdot c_g - k_g(\text{theor})[1 - 0.25] \cdot c_g \\ & = [k_g(\text{expt}) - 0.75 \cdot k_g(\text{theor})] \cdot c_g \quad \text{-----(3)} \end{aligned}$$

where $k_g(\text{expt})$ = experimental (gaseous + particulate) mass transfer coefficient

$k_g(\text{theor})$ = theoretical (gaseous) mass transfer coefficient

Therefore equating equations (2) and (3) we get:

$$k_g(\text{expt}) - 0.75 \cdot k_g(\text{theor}) = \frac{(2)(0.25) \cdot D_p^2 \cdot \rho_p \cdot \pi^2 \cdot n^2 \cdot R}{9 \cdot \mu}$$

This allows, after rearranging, the determination of the particulate size factor $D_p^2 \cdot \rho_p$ such that:

$$D_p^2 \cdot \rho_p = \frac{[k_g(\text{expt}) - 0.75 \cdot k_g(\text{theor})] 9 \cdot \mu}{(2)(0.25) \cdot \pi^2 \cdot n^2 \cdot R}$$

And since $k_g(\text{expt}) = 55 \pm 13 \text{ m h}^{-1}$ and $k_g(\text{theor}) = 66 \pm 10 \text{ m h}^{-1}$

then the expected (most likely) value of $D_p^2 \cdot \rho_p$ is:

$$\begin{aligned} D_p^2 \cdot \rho_p & = \frac{[55 - 0.75(66)](9)(2.156 \times 10^{-5})}{(3600)(0.25)(\pi^2)(1050/60)^2(28.1 \times 10^{-3})} \\ & = 7.3 \times 10^{-9} \text{ kg m}^{-1} \end{aligned}$$

By taking ρ_p between 1000 and 2000 kg m^{-3} then:

$$D_p = 1.9 \text{ to } 2.7 \text{ micrometres}$$

The maximum value of $D_p^2 \cdot \rho_p$ (by taking $k_g(\text{expt}) = 55 + 13 = 68 \text{ m h}^{-1}$ and $k_g(\text{theor}) = 66 - 10 = 56 \text{ m h}^{-1}$) is:

$$D_p^2 \cdot \rho_p = \frac{[68 - 0.75(56)](9)(2.156 \times 10^{-5})}{(3600)(0.25)(\pi^2)(1050/60)^2(28.1 \times 10^{-3})}$$

$$= 3.45 \times 10^{-8} \text{ kg m}^{-1}$$

By taking ρ_p between 1000 and 2000 kg m^{-3} then:

$$D_p(\text{max}) = 4.1 \text{ to } 5.9 \text{ micrometres}$$

Part 2

By using the value of $D_p^2 \cdot \rho_p$ an estimate of the collection efficiency of water drops can be obtained (38).

e.g.

For a water drop of diameter $0.5 \times 10^{-3} \text{ m}$ falling at its terminal velocity of 2.2 m s^{-1} in a particulate laden gas at 96°C , the impaction parameter (K) is:

$$K = \frac{v_d \cdot D_p^2 \cdot \rho_p}{9 \cdot \mu \cdot D_d}$$

where v_d = velocity of drop

D_d = diameter of drop

μ = viscosity of carrier gas

$D_p^2 \cdot \rho_p$ = particulate size factor (see part 1)

i.e.

$$K = \frac{(2.2)(7.3 \times 10^{-9})}{(9)(2.156 \times 10^{-5})(0.5 \times 10^{-3})}$$

$$= 0.165$$

Using the results of Walton and Woolcock (38) this corresponds to a collection efficiency, $E \approx 0.02$. i.e. 2% of the particulates in the path of the drop are collected. (Using the maximum value of $D_p^2 \cdot \rho_p$ determined above, the maximum collection efficiency is 28%).

By calculating the mass transfer rates for both the particulate and gaseous components of the gas stream, using the same drop size as above (0.5×10^{-3} m diameter), it can be determined which is the limiting component for the liquid to gas ratio required for adequate scrubbing.

PARTICULATE COMPONENT:

$$\text{Mass transfer rate, } M(\text{part}) = E \cdot V_d \cdot N \cdot m_F$$

where E = collection efficiency

$$\begin{aligned} V_d &= \text{volume swept out by drop} \\ &= (\pi/4) \cdot D_d^2 \cdot v_d \end{aligned}$$

N = number concentration of particles

m_F = mass of fluoride per particle

$$\begin{aligned} \text{Therefore } M(\text{part}) &= E \cdot (\pi/4) \cdot D_d^2 \cdot v_d \cdot N \cdot m_F \\ &= E \cdot (\pi/4) \cdot D_d^2 \cdot v_d \cdot 0.25 \cdot c_g \quad (\text{since } N \cdot m_F = 0.25 c_g) \end{aligned}$$

$$\text{Now } E = 0.02 ; \quad D_d = 0.5 \times 10^{-3} \text{ m} ; \quad v_d = 2.2 \text{ m s}^{-1}$$

$$\text{and let } c_g = 10000 \text{ mg F m}^{-3}$$

$$\begin{aligned} \text{Therefore } M(\text{part}) &= (0.02)(\pi/4)(0.5 \times 10^{-3})(2.2)(0.25)(10000) \\ &= 2.16 \times 10^{-5} \text{ mg F s}^{-1} (\text{drop})^{-1} \end{aligned}$$

For the sake of argument, let us take a horizontal duct of cross section 1 m x 1 m, with spray nozzles spraying water down from its roof. If a water drop falls through a distance of 1 metre then the drop residence time is $1/v_d = 1/2.2$ s. In this time the drop will collect:

$$\begin{aligned} &2.16 \times 10^{-5} / 2.2 \\ &= 9.81 \times 10^{-6} \text{ mg F (drop)}^{-1} \end{aligned}$$

In order to collect 99% of the particulate fluorides (i.e. $0.99 \times 2500 \text{ mg F m}^{-3}$) the volume of water required is:

$$\begin{aligned} &[(0.99)(2500)/9.81 \times 10^{-6}] [(1/6) \cdot \pi \cdot (0.5 \times 10^{-3})^3] \\ &= 0.0165 \text{ m}^3(\text{H}_2\text{O}) \text{ m}^{-3}(\text{gas}) \end{aligned}$$

i.e. 16.5 litres of water per cubic metre of gas is required to remove 99% of the particulate fluorides present. (Using the maximum value for $D_p^2 \cdot \rho_p$ given above, having a collection efficiency of 28%, the minimum quantity of water required to remove 99% of the particulate fluorides per cubic metre of gas is 1.2 litres).

GASEOUS COMPONENT:

$$\text{Mass transfer rate, } M(\text{gas}) = k_{g,d} \cdot A \cdot (1 - 0.25) \cdot c_g$$

assuming $k_{g,d}$ is constant and the fluoride vapour pressures are negligible

where $k_{g,d}$ = mass transfer coefficient for the drop
 A = liquid-gas interfacial area of the drop
 c_g = total (gaseous + particulate) fluoride concentration

From Koval et al (22) $k_{g,d} = 253 \text{ m h}^{-1}$ for $4.1 \times 10^{-3} \text{ m}$ diameter drops at 20°C falling at their terminal velocity. This was found to check with theoretical calculations (appendix 8, part 1). Therefore from similar calculations (appendix 8, part 2) a value for $k_{g,d}$ for $0.5 \times 10^{-3} \text{ m}$ drops falling at their terminal velocity through air at 96°C was found to be $\approx 685 \text{ m h}^{-1}$.

Therefore, for $c_g = 10000 \text{ mg F m}^{-3}$

$$\begin{aligned} M(\text{gas}) &= (685/3600) \pi \cdot (0.5 \times 10^{-3})^2 (0.75) (10000) \\ &= 1.12 \times 10^{-3} \text{ mg F s}^{-1} (\text{drop})^{-1} \end{aligned}$$

To collect 99% of the gaseous fluorides in the above duct (using a calculation similar to that above for particulates) approximately 0.95 litres of water per cubic metre of gas is required.

COMPARISON

The liquid to gas ratio (L/G) required to collect the gaseous fluorides can be reduced appreciably by scrubbing with

smaller water droplets, but, the liquid to gas ratio for the particulate component will be relatively unaffected (38)

e.g.

For 0.25×10^{-3} m diameter drops falling at their terminal velocity of 0.8 m s^{-1} :

gaseous component : $L/G = 0.17$ (cf. $L/G = 0.95$ above)

particulate component: $L/G = 16.5$ (cf. $L/G = 16.5$ above)

Therefore, at least in gravity-dominated sprays in ducts, it can be said that the particulate component is the limiting component in determining the liquid to gas ratio required to achieve adequate scrubbing.

Part 3

Determination of the maximum scrubber liquor concentration obtainable in the above duct, using the liquid to gas ratio required to remove 99% of the particulate fluorides.

i.e.

$$\begin{aligned} L/G = 16.5 \quad \text{for } D_p^2 \cdot \rho_p \cdot c_g &= 7.3 \times 10^{-9} \text{ kg m}^{-1} \\ c_g &= 10000 \text{ mg F m}^{-3} \\ D_d &= 0.5 \times 10^{-3} \text{ m} \\ \text{particulate concentration} &= 25\% \end{aligned}$$

Particulate component:

Particulate concentration is: 2500 mg F m^{-3} . Therefore in order to collect 99% of these particulates the L/G ratio of 16.5 must be used and hence the liquor concentration obtainable is:

$$\begin{aligned} \text{Liquor concentration (part)} &= (2500)(0.99)/16.5 \\ &= 150000 \text{ mg F m}^{-3} (\text{H}_2\text{O}) \\ &= 0.015\% \text{ F (w/w)} \end{aligned}$$

Gaseous component :

Gaseous concentration is: 7500 mg F m^{-3} [$\approx 0.75\% \text{ F (w/w)}$]. Therefore from a simple mass balance along the duct at steady

state conditions the maximum liquor concentration possible is:

$$\begin{aligned}\text{Liquor concentration (gas)} &= 0.75/16.5 \\ &= 0.045\% \text{ F (w/w)}\end{aligned}$$

Therefore the total fluoride concentration attainable under these conditions is:

$$\begin{aligned}\text{Liquor concentration (total)} &= 0.015 + 0.045 \\ &= 0.06\% \text{ F (w/w)}\end{aligned}$$

Appendix 7

The Influence of the Rotation Speed of the Sample Cylinder
on the Gaseous and Particulate Fluoride Absorption

At 1050 rpm of the sample cylinder and with 25% particulate concentration in the gas stream;

$$k_g(\text{expt}) = 55 \text{ m h}^{-1}$$

$$\begin{aligned} \text{and the effective } k_g(\text{gas}) &= 0.75.k_g(\text{theor}) = (0.75)(66) \\ &= 49.5 \text{ m h}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Therefore } k_g(\text{part}) &= 55 - 49.5 \\ &= 5.5 \text{ m h}^{-1} \end{aligned}$$

Or $(5.5/55)(100) = 10\%$ particulate fluoride component in the absorption

At twice the rotation speed of the sample cylinder i.e. 2100 rpm

$$\begin{aligned} k_g(\text{theor}) &= (2100/1050)^{0.8} \cdot (66) \quad (\text{appendix 5}) \\ &= 114.9 \text{ m h}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Therefore } k_g(\text{gas}) &= 0.75.k_g(\text{theor}) \\ &= 86.2 \text{ m h}^{-1} \end{aligned}$$

Now from appendix 6, part 1

$$D_p^2 \cdot \rho_p = \frac{[k_g(\text{expt}) - 0.75.k_g(\text{theor})]9.\mu}{(2)(0.25).\pi^2.n^2.R}$$

Therefore

$$\begin{aligned} k_g(\text{expt}) &= 0.75.k_g(\text{theor}) + \frac{(2)(0.25)D_p^2 \cdot \rho_p \cdot \pi^2 \cdot n^2 \cdot R}{9.\mu} \\ &= 0.75.(114.9/3600) \\ &\quad + \frac{(2)(0.25)(7.3 \times 10^{-9})(\pi^2)(2100/60)^2.(28.1 \times 10^{-3})}{9.(2.156 \times 10^{-5})} \\ &= 0.030 \text{ m s}^{-1} \\ &= 108.2 \text{ m h}^{-1} \end{aligned}$$

Therefore $k_g(\text{part}) = 108.2 - 86.2$
 $= 22 \text{ m h}^{-1}$

Or $(22.0/108.2)(100) \approx 20\%$ particulate fluoride component in the
absorption

i.e. At twice the rotation speed both the gaseous and particulate fluoride mass transfer rates increased, with the particulate component increasing faster than the gaseous (The particulate component increased 4 fold, whereas the gaseous component almost doubled).

Appendix 8, part 1

Theoretical Check on the Validity of the Mass Transfer
Coefficient given by Koval et al for the Absorption
of Silicon Tetrafluoride in Water Drops (4.1 mm ϕ)

To calculate theoretically the mass transfer coefficient for the absorption into water drops the following reference was used and the following assumptions were made:

Reference :

Clift, R; Grace, J. R; Weber, M. E; Bubbles Drops and Particles, Academic Press, New York (1978)

Assumptions:

- (1) The diameter given is the volume equivalent diameter, D_d
i.e. $D_d = (6.V/\pi)^{1/3} = 4.1 \times 10^{-3}$ m
- (2) Koval et al carried out their experimental determination at atmospheric pressure and at a temperature of 20 °C.
- (3) The liquid drop and SiF_4 gas behave as pure water and dry air respectively.
- (4) The water drop fell under the influence of gravity only.
- (5) The internal resistance of the drop to mass transfer is negligible. i.e. absorption is gas phase controlled.

CALCULATION OF THE TERMINAL VELOCITY OF THE WATER DROP IN AIR

$$\text{Eotvos number, } E_o = g \cdot (\rho_d - \rho) \cdot D_d^2 / \sigma$$

$$\begin{aligned} \text{where } g &= \text{acceleration due to gravity} = 9.81 \text{ m s}^{-2} \\ \rho_d &= \text{density of drop} = 998.2 \text{ kg m}^{-3} @ 20 \text{ }^\circ\text{C} \\ \rho &= \text{density of gas} = 1.207 \text{ kg m}^{-3} @ 20 \text{ }^\circ\text{C} \\ D_d &= \text{water drop diameter} = 4.1 \times 10^{-3} \text{ m} \\ \sigma &= \text{surface tension of water} = 72.8 \times 10^{-3} \text{ N m}^{-1} \end{aligned}$$

$$\text{Therefore } E_o = 2.258$$

$$\text{Morton number, } M_o = g \cdot \mu^4 \cdot (\rho_d - \rho) / \rho^2 \cdot \sigma^2$$

$$\begin{aligned} \text{where } \mu &= \text{viscosity of gas} \\ &= 1.812 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} \text{ @ } 20 \text{ }^\circ\text{C} \end{aligned}$$

$$\text{Therefore } M_o = 1.876 \times 10^{-12}$$

$$\text{Now for } 1.84 \leq E_o \leq 5.0$$

$$\begin{aligned} Re &= 1.83 \cdot E_o^{0.555} \cdot M_o^{-0.25} \\ &= (1.83)(2.258)^{0.555} \cdot (1.876 \times 10^{-12})^{-0.25} \\ &= 2457.3 \end{aligned}$$

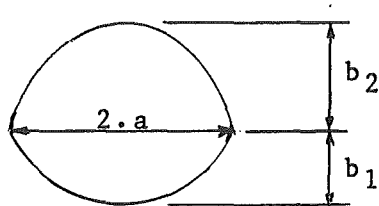
Therefore the terminal velocity (v_d) is:

$$\begin{aligned} v_d &= Re \cdot \mu / \rho \cdot D_d \\ &= (2457.3)(1.812 \times 10^{-5}) / (1.207)(4.1 \times 10^{-3}) \\ &= 9.0 \text{ m s}^{-1} \end{aligned}$$

SHAPE OF THE DROP FALLING THROUGH THE AIR AND ITS SURFACE AREA

The shape of the drop can be represented by two oblate semi spheroids with a common semimajor axis, a , and minor semiaxes b_1 and b_2 .

i.e.



The values of a , b_1 and b_2 can be determined by the following:

$$\text{For } 0.5 < E_o < 8$$

$$\begin{aligned} \text{The aspect ratio } \frac{b_1 + b_2}{2 \cdot a} &= \frac{1.0}{1.0 + 0.18 \cdot (E_o - 0.4)^{0.8}} \\ &= 0.77 \end{aligned}$$

and;

$$\begin{aligned} \text{the shape factor } \frac{b_1}{b_1 + b_2} &= \frac{1.0}{1.0 + 0.12 \cdot (E_o - 0.5)^{0.8}} \\ &= 0.42 \end{aligned}$$

From geometric considerations:

$$D_d/a = 2 \cdot [(b_1 + b_2)/2 \cdot a]^{1/3}$$

Therefore

$$\begin{aligned} a &= \frac{D_d}{2 \cdot [(b_1 + b_2)/2 \cdot a]^{1/3}} \\ &= 2.254 \times 10^{-3} \text{ m} \quad (\text{or } 2 \cdot a = 4.47 \times 10^{-3} \text{ m}) \end{aligned}$$

Thus $\frac{b_1 + b_2}{2 \cdot a} = 0.77$

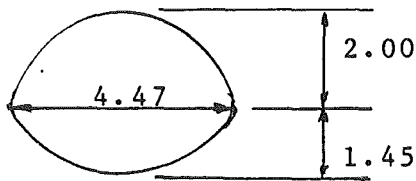
$$\begin{aligned} \Rightarrow b_1 + b_2 &= (0.77)(4.47 \times 10^{-3}) \\ &= 3.44 \times 10^{-3} \text{ m} \end{aligned}$$

And $\frac{b_1}{b_1 + b_2} = 0.42$

$$\begin{aligned} \Rightarrow b_1 &= (0.42)(3.44 \times 10^{-3}) \\ &= 1.45 \times 10^{-3} \text{ m} \end{aligned}$$

$$\begin{aligned} \Rightarrow b_2 &= 3.44 \times 10^{-3} - 1.45 \times 10^{-3} \\ &= 2.00 \times 10^{-3} \text{ m} \end{aligned}$$

Therefore the dimensions of the drop are (in mm):



The surface area (A) is given by:

$$A = 2 \cdot \pi \cdot a^2 + \pi / 2 \cdot [b_1^2 / e_1 \cdot \ln(X_1) + b_2^2 / e_2 \cdot \ln(X_2)]$$

$$\text{where } e_1 = [1 - (b_1/a)^2]^{0.5} = 0.76$$

$$e_2 = [1 - (b_2/a)^2]^{0.5} = 0.45$$

$$X_1 = (1 + e_1)/(1 - e_1) = 7.33$$

$$X_2 = (1 + e_2)/(1 - e_2) = 2.64$$

Therefore $A = 5.38 \times 10^{-5} \text{ m}^2$

MASS TRANSFER COEFFICIENT CALCULATION

For liquid drops in gases at low pressure the equation for solid particles is used to predict the external mass transfer rates:

$$\frac{Sh' - Sh'_0/2}{Sc^{1/3}} = 0.62 \cdot (1 - z)^{1/2} \cdot (Re')^{1/2} + 0.056 \cdot (z \cdot Re')^{0.71}$$

$$\text{for } 1000 < Re' < 100000$$

The superscript ' implies that the dimensionless group is based on the length, L'

$$\begin{aligned} \text{Where } L' &= \frac{\text{surface area of the drop}}{\text{maximum perimeter projected on a plane normal to flow}} \\ &= A/2\pi \cdot a = 5.38 \times 10^{-5} / 2\pi \cdot (2.24 \times 10^{-3}) \\ &= 3.82 \times 10^{-3} \text{ m} \end{aligned}$$

$$Sh' = \text{Sherwood number} = k_{g,d} \cdot L' / D'$$

$$\begin{aligned} Sh'_0 &= \text{Sherwood number for diffusion into a stagnant medium} \\ &\approx 2.0 \end{aligned}$$

$$\begin{aligned} Sc &= \text{Schmidt number} \\ &= \mu / \rho \cdot D' \quad D' = \text{diffusivity} = 9.9 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \quad (22) \\ &= 1.812 \times 10^{-5} / (1.207)(9.9 \times 10^{-6}) \\ &= 1.52 \end{aligned}$$

$$\begin{aligned} Re' &= \text{Reynolds number} \\ &= \rho \cdot v_d \cdot L' / \mu \\ &= (1.207)(9.0)(3.82 \times 10^{-3}) / (1.812 \times 10^{-5}) \\ &= 2290 \end{aligned}$$

$$\begin{aligned} z &= \text{fraction of particle surface area aft of the maximum} \\ &\quad \text{perimeter in a plane normal to the flow} \\ &= \{ \pi \cdot a^2 + \pi / 2 \cdot [b_2^2 / e_2^2 \cdot \ln(X_2)] \} / A \\ &= 0.54 \end{aligned}$$

Therefore

$$\begin{aligned} \frac{Sh' - Sh'_0/2}{Sc^{1/3}} &= 0.62(1 - 0.54)^{1/2} \cdot (2290)^{1/2} + 0.056 \cdot (0.54 \times 2290)^{0.71} \\ &= 28.91 \end{aligned}$$

Hence

$$\begin{aligned} Sh' &= (28.91)(1.52)^{1/3} + 1 \\ &= 34.24 \end{aligned}$$

$$\begin{aligned} \text{So } k_{g,d} &= (34.24)(9.9 \times 10^{-6}) / (3.82 \times 10^{-3}) \\ &= 0.089 \text{ m s}^{-1} \\ &= 319 \text{ m h}^{-1} \end{aligned}$$

The experimentally determined value of $k_{g,d}$ by Koval et al is 253 m h^{-1} . Therefore the error between this value and that determined theoretically above is $\sim 25\%$, which is considered a reasonable agreement. Hence it should be possible to use the theory to predict the mass transfer coefficient for drops of different sizes and at different gas temperatures, when absorbing SiF_4 .

Part 2

Calculation of the Mass Transfer Coefficient for the Absorption of SiF_4 at 96°C into Water Drops 0.5 mm Diameter

Since the experimental mass transfer coefficient found by Koval et al (22) checks with theoretical calculations (part 1) a similar calculation can be used to determine the mass transfer coefficient for smaller drops ($D_d = 0.5 \times 10^{-3} \text{ m}$) falling at their terminal velocity ($v_d = 2.2 \text{ m s}^{-1}$) at a higher gas temperature (96°C).

$$\begin{aligned} \text{i.e. } Re &= v_d \cdot D_d / \nu & \text{where } \nu &= 2.254 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} @ 96^\circ\text{C} \\ &= 48.8 \end{aligned}$$

$$\begin{aligned} Sc &= \nu / D' & \text{where } D' &= 1.40 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} @ 96^\circ\text{C} \\ &= 1.61 \end{aligned}$$

From Clift et al (7): For $1 < Re < 100$

$$\begin{aligned} (Sh - 1) / Sc^{1/3} &= [1 + (1/Re \cdot Sc)]^{1/3} \cdot Re^{0.41} \\ &= 4.94 \end{aligned}$$

Therefore $Sh = 6.79$ and hence $k_{g,d} = 685 \text{ m h}^{-1}$

Appendix 9

Comparison of the Rate of Heat Transfer to a Water Drop by the
Condensation of Water Vapour to the Rate of Heat Transfer by
Conduction away from a Water Drop

By comparing these two heat transfer rates it can be determined whether the introduction of "cool" water drops into a "hot" gas stream will cause the gas to cool with an increase in the size of the particulate fluorides present, due to water vapour condensing around them, or with an increase in the size of the water drops, again due to condensation, or both. If the particulates increase in size then this will result in an improved collection efficiency by the water drops and hence the removal of fluorine may become limited by the absorption of the gaseous fluoride component.

We will assume the following: (1) The water drop is 0.5 mm diameter and at 20 °C. (2) The "gas" stream is saturated and at 96 °C. (3) The Nusselt number, Nu, and Sherwood number, Sh, for heat and mass transfer, respectively, can both be taken as being equal to 2, i.e. for transfer into a stagnant medium.

Now $Q_{\text{condens}} = L \cdot m \approx L \cdot k_{g,w} \cdot c_w$

assuming the vapour pressure of water at the drop is negligible

where Q_{condens} = heat transfer flux due to condensation

L = latent heat

$k_{g,w}$ = mass transfer coefficient for water vapour

c_w = concentration of water vapour in the "gas" stream

Since $Sh = 2$ and the diffusion coefficient for water vapour in air at 96 °C is $3.0 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, then:

$$\begin{aligned} k_{g,w} &= (2)(3.0 \times 10^{-5}) / (0.5 \times 10^{-3}) \\ &= 0.12 \text{ m s}^{-1} \quad (= 437 \text{ m h}^{-1}) \end{aligned}$$

Also at 96 °C; the water vapour concentration, $c_w = 2.295 \text{ kg(H}_2\text{O) m}^{-3}$ (gas), and the latent heat, $L = 1348 \text{ kJ kg}^{-1}$ (H₂O).

$$\begin{aligned}\text{Therefore } Q_{\text{condens}} &= (1348)(0.12)(2.295) \\ &= 371.2 \text{ kW m}^{-2}\end{aligned}$$

$$\text{Now } Q_{\text{conduct}} = h_w(T_w - T_g)$$

where Q_{conduct} = heat transfer flux due to conduction
 h_w = heat transfer coefficient for water vapour
 T_g = temperature of gas stream
 T_w = temperature of water drop

Since $Nu = 2$ and the thermal conductivity for water vapour in air at 96 °C is $24.4 \times 10^{-6} \text{ kW m}^{-1} \text{ K}^{-1}$, then:

$$\begin{aligned}h_w &= (2)(24.4 \times 10^{-6}) / (0.5 \times 10^{-3}) \\ &= 0.10 \text{ kW K}^{-1} \text{ m}^{-2}\end{aligned}$$

$$\begin{aligned}\text{Therefore } Q_{\text{conduct}} &= (0.10)(20 - 96) \\ &= -7.4 \text{ kW m}^{-2}\end{aligned}$$

Thus the transfer of heat to the water drop by condensation is approximately 50 times greater than the conduction of "negative" heat to the gas. This implies that cool water drops when introduced into a gas stream are more likely to increase in size, due to the condensation of water vapour around them, than to cool the gas and allow the water vapour to condense around the particulates present.