FL 034

SUPPLEMENTAL DATA FOR PSD REVIEW

FL-034

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

DECEMBER 14, 1979

SHOLTES & KOOGLER
Environmental Consultants
1213 NW 6TH ST ■ GAINESVILLE, FL 32601 ■ 904-377-5822

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1.0 COOLING POND/GYPSUM STACK

1.1 Introduction

The purpose of this section is to address the potential of fugitive fluoride emissions from the cooling water pond at the New Wales Chemical Complex as a result of the proposed expansion. The chemistry of the cooling pond/gypsum stack is discussed with emphasis on fluoride chemistry. Sources of fluorides in the pond, other than the phosphoric acid plant are included. Literature on fluoride emissions from the ponds are cited and the factors influencing fluoride emissions are discussed. These materials are combined to develop an estimate of increased fluoride emissions from the pond resulting from the proposed expansion. Control techniques are evaluated.

In reviewing this section it should be realized that New Wales will not have to increase the surface area of the present cooling pond beyond the present 300 acres or increase the quantity of water in the pond beyond the present 2.4×10^9 gallons as a result of the proposed expansion. Neither will the chemistry of the pond be altered.

Based upon information presented herein, it is the position of New Wales that the actual increase in fluoride emissions resulting from the proposed expansion including increased emissions from the cooling pond will be less than 50 tons per year.

1.2 Process Chemistry

The most common method of producing phosphoric acid is by a wet process utilizing phosphate rock and sulfuric acid. The use of this process is the reason for the existence of the gypsum stack. The pond commonly associated with the system functions as a reservoir for process water and a cooling system for this water. The term sometimes applied to this system is a "gypsum pond". In reality, the system is a cooling pond and a gypsum stack and in this text it is referred to as a cooling pond/gypsum stack.

Phosphate rock is a complex material; the principal mineral constituent, fluorapatite, contains calcium, phosphate, fluoride, carbonate and many other elements or groups bound together in a crystal lattice. When the rock is treated with a strong mineral acid, the apatite lattice is destroyed and the phosphate constituent is converted to phosphoric acid. The overall reaction with sulfuric acid is as follows:

1. The tricalcium phosphate constituent is converted to phosphoric acid and calcium sulfate:

   $$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4 ,$$

2. The calcium fluoride constituent of the fluorapatite reacts with sulfuric acid to produce hydrogen fluoride and calcium sulfate:

   $$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 ,$$

3. The calcium carbonate constituent is converted to carbon dioxide and calcium sulfate:

   $$CaCO_3 + H_2SO_4 \rightarrow CO_2 + CaSO_4 + H_2O .$$

The excess fluoride present in the phosphate rock also reacts with phosphoric acid to form HF:

$$CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HF .$$

The HF then reacts with excess silica:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O .$$

During the acid concentration steps a considerable portion of the fluosilicic acid dissociates to form HF and SiF_4:

$$H_2SiF_6 \rightleftarrows SiF_4 + 2HF$$

The fumes resulting from H_2SiF_6 volatilization are scrubbed with water; however, regenerating the H_2SiF_6:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

$$SiO2 + 6HF \rightarrow H2SiF_6 + 2H_2O$$

which is pumped to the pond with the gypsum slurry.

It should be pointed out that the above reactions greatly simplify the reactions occurring during the digestion of phosphate rock and the subsequent behavior of various materials, particularly fluorides in the product acid and in the water used for filter washing and sluicing the gypsum to the gypsum stack.

The pond/stack is a vital unit process in the typical, highly integrated phosphoric acid and fertilizer manufacturing complex. It serves not only the wet process phosphoric acid facilities, but also the many fertilizer manufacturing processes which are dependent on phosphoric acid as a feed stock. The pond/stack is a source of cooling water, scrubber water, wash water, process water and slurry water; a water pollution control and water conservation process operation; and a disposal area for gypsum.

In the digestion of the phosphate rock with sulfuric acid, a weak phosphoric acid-gypsum slurry is produced. The gypsum is filtered, slurried with pond water and pumped to the gypsum disposal area. The phosphoric acid containing 26-30 percent P_2O_5 is then evaporated to 40-50 percent P_2O_5. The digestion and evaporation results in the discharge of approximately 70 percent of the fluoride content of the rock to the pond/stack; approximately 40 percent in water used in the evaporator barometric condensers and scrubbers and 30 percent in the gypsum. If the same plant also produces DAP, part of the fluoride in the phosphoric acid will also pass to the pond with the scrubber water used in this process. Thus, 70 percent or more of the fluoride originally present in the phosphate rock may find its way to the pond/stack.

The water of the pond is normally acid, having a pH around 1.5. This acidity is primarily due to inclusion of phosphoric acid in the washed gypsum from the gypsum filter and secondarily to fluosilicic acid ($H2SiF_6$) and hydrofluoric acid (HF). Pond/stack systems from around the country have been found to have a fluoride concentration of 2,000-12,500 ppm depending upon the solibility of the various fluoride compounds in the system. The fluoride concentration of the New Wales pond is 8,000-9,000 ppm. The fluoride concentration of a given pond does not continue rising, but tends to stabilize over a period of three to five years. The reason for this stabilization and the fluoride level at which a given pond will stabilize is addressed in a paper by Lehr (Attachment 1).

In this paper Lehr identifies 12 fluoride compounds present in a pond/stack system and suggests there are probably more. The presence of these compounds, and the relative concentrations, depend upon the presence of several cations including Al, Mg, Na, Si and to a lesser degree Ca and K.

One very important fact brought out in the Lehr paper is the variation in the solubility of the various fluoride compounds in 30 percent phosphoric acid (acid from the filters), in sluice water and in pond water. Lehr shows the solubility of some of the most prevalent fluoride species to be 16 times greater in pond water than in 30 percent acid.

The effect of this is that fluoride compounds precipitated in the digester and filter and transported to the pond/stack with the gypsum will dissolve in the pond water because of the greater solubility in this medium. A further implication is that the recovery of fluoride from the evaporator condensate as fluosilicic acid will not have any effect on the concentration of fluorides in the pond water since the same equilibrium will be reached as a result of the dissolution of fluorides in the gypsum.

As an example of this, it was reported(1) that the fluoride concentration in the pond/stack system of a plant that has always recovered fluoride from the phosphoric acid evaporator system average 10,000 ppm. In the New Wales pond/stack system, the fluoride concentration averages 8000-9000 ppm and fluoride recovery has never been practiced.

1.3 Fluoride Emissions

Emissions of volatile hydrogen fluoride and silicon tetrafluoride from the pond/stack have been the subject of numerous studies. A recent EPA report presents a critical review of the major studies reporting gypsum pond fluoride emissions(2).

After close scrutiny of the data, emissions from cooling ponds were found to range from 0.1 to 10 pounds per acre-day with an average value of 2.0 pounds per acre-day.

At the end of August 1977, a field program was carried out near Bartow, Florida, with the cooperation of EPA to measure fluoride emissions from a cooling pond(3). Average fluoride emission rates from the pond were estimated to be in the range of 2 to 3 pounds per acre-day. Data collected by remote optical sensing indicate that fluoride emissions from the gypsum pond consisted entirely of hydrogen fluoride (HF). The silicon tetrafluoride (SiF_4) concentration was below the detectable threshhold of 0.5 ppb. It is interesting to note that Lehr predicted that the predominant gaseous fluoride compound emitted from a pond would be HF. He predicted that in a pond with a fluoride concentration of 10,000 ppm the ratio of $HF:SiF_4$ in the vapor phase would be in the range of 100:1.

The implication of the information presented thus far is quite significant when one attempts to assess the impact of increased phosphoric acid production and increased pond water usage for scrubbers on fluoride emissions from pond/stack systems. Similar implications exist when one considers techniques for controlling emissions from the pond/stack.

It has been reported in many sources and observed in all pond/stack systems that fluoride levels in pond water reach an equilibrium in three to five years. In the case of New Wales, an equilibrium of 8000-9000 ppm was reached in three years (Attachment 2).

It follows from information in Lehr's paper and the fact that if additional fluorides are added to the system, either with the gypsum or in pond water, the equilibrium will persist and the added fluorides will precipitate. This assumes, of course, that essentially the same sources of fluorides and other ions are involved; i.e., that the chemistry of the system is not changed. In the case of New Wales, the chemistry of the system will not change with the proposed expansion since only additional phosphoric acid capacity and additional DAP capacity will be added. Both types of sources presently exist.

or vaporize

If; therefore, the pond chemistry does not change, and the surface area of the pond does not change, the fluoride emissions from the pond will increase only as a result of the pond water temperature increase and the effect this increase has on the vapor pressure of the HF-pond water system. According to Tatera(4), an increase in pond water temperature of 1°F in the 95°F temperature range will result in a three percent increase in fluoride vapor pressure; and hence a three percent increase in fluoride emissions, other factors remaining constant (Figure 1).

The expansion proposed by New Wales will result in an increase in the heat load to the pond of approximately 0.3×10^9 BTU per hour. The present heat load to the pond is approximately 1.0×10^9 BTU per hour. This increase in the heat load will result from an increase in the water flow rate through the pond; not in an increase in the inlet water temperature. The pond exit temperature will not change either since the pond is of sufficient size to allow the pond water temperature to reach equilibrium under existing and proposed conditions. Since the initial and final temperature in the pond will not change the additional heat load will be reflected by an increase in the surface area necessary to reach the equilibrium temperature.

It was calculated [(5) and Attachment 3] that under present conditions and with the pond temperature at the highest level observed at New Wales (112°F inlet and 92°F outlet) a surface area of 204 acres is required to achieve the 20°F temperature reduction (112° - 90° = 20°F). It should be noted that 20°F is the typical temperature differential across the pond.

Under proposed conditions a surface area of 246 acres would be required to achieve this temperature drop. Both areas are less than the present pond area of 300 acres (Figure 2).

Using the vapor pressure data of Tatera (Figure 1) and the method of calculating heat release to the atmosphere previously referenced(5), the pond areas necessary to achieve 1°F temperature decreases from 112°F to 92°F were calculated for existing and proposed conditions(Attachment 3).

According to various studies(2), the fluoride emissions from ponds depend primarily upon the vapor pressure of fluoride, wind speed and pond area. The HF vapor pressure takes into account fluoride concentration and temperature. To estimate the increase in pond fluoride emissions from the expansion proposed by New Wales, it was assumed that the wind speed would be constant. The change in emissions will therefore be proportional to the change in the product of the pond area and the fluoride vapor pressure.

Since the fluoride vapor pressure varies across the pond as a function of temperature a numeric integration was carried out using the areas necessary to achieve the 1°F temperature decreases and the vapor pressure corresponding to the temperature of each of those areas. An initial pond water temperature of 112°F and an equilibrium temperature of 92°F were assumed; the maximum temperatures recorded at New Wales.

Using this approach it was determined that the increase in fluoride emissions from the New Wales pond as a result of the proposed expansion would be 3.2 percent.

If one assumes a fluoride emission factor for ponds of 2.0 pounds per acre per day, the fluoride emission rate from the existing New Wales 300-acre pond is in the range of 110 tons per year. A 3.2 percent increase resulting from the proposed expansion will result in an increase in this fluoride emission rate of 3.5 tons per year.

If one assumes the most severe fluoride emission rate from a pond of 10 pounds per acre per day the annual emissions would be approximately 548 tons per year and the increase will be 17.5 tons of fluoride per year.

Even this maximum increase, when combined with the actual increase in fluoride emissions from the proposed phosphoric acid plant, DAP plant and other "new" sources of 28.4 tons per year will result in a total increase in actual fluoride emissions of only 45.9 tons per year. This increase is less than 50 tons per year and establishes fluorides as a minor pollutant requiring a Tier I review. In view of this, other discussions of fluoride control will be limited to Tier I requirements of current PSD regulations.

1.4 Control of Fluoride Emissions From The Pond/Stack

Before discussing the control of fluoride emissions from the cooling pond/gypsum stack, a brief review of the environmental significance of the emissions is in order.

In the source assessment document of the phosphate fertilizer industry(6) a "severity factor" is defined. It is defined as "the ratio of the time-averaged maximum ground-level concentration of a pollutant to a hazard factor. ...for fluoride..., it (the hazard factor) is a reduced threshold limit value". For fluoride, the reduction in the threshold limit value takes into consideration a 24-hour exposure and a safety factor of 100.

Using the criteria set forth in the source assessment document(6), the severity factor for pond fluoride emissions at the nearest New Wales property line is 0.11. At the nearest property owned by non-phosphate interests, the severity factor is 0.07(Figure 3). This severity factor relates to a 24-hour ground-level fluoride concentration of approximately 0.7 ug/m^3. The Fluoride standard for a 24-hour period adopted by several states is in the range of 2.9 ug/m^3; over four times the concentration expected from the New Wales pond.

Another consideration is that of observed fluoride effects in the vicinity of cooling ponds. As one phase of an EIS for a phosphate fertilizer plant [(7)and Attachment 4] the effects of fluorides on vegetation, cattle, timber and ambient air were observed. It was concluded that no adverse economic effects resulted from fluoride emissions from the existing chemical complex; including phosphoric acid plants, granular products plants (DAP, GTSP) and a cooling pond/gypsum stack.

The control of fluoride emissions from New Wales cooling ponds/gypsum stacks, if required by current PSD regulations, will result in no significant improvement to the environment since ambient levels are already below typical air quality standards and adverse environmental effects do not presently exist.

In the preceding section, it was shown that fluoride recovery in the phosphoric acid evaporator system will have no influence on fluoride levels in the pond water and, hence, no influence on fluoride emissions from the pond/stack. This conclusion is contrary to that in other published reports(2), but is well supported by theory and observation.

Other methods of controlling fluoride emissions from ponds which have been addressed(2) include liming, transporting gypsum by conveyor (a dry stack), calcining the phosphate rock to defluorinate prior to acidulating and process modifications.

The use of liming for pH control would be very effective for reducing fluoride emissions. An increase in pH from 1.4 to 3.9 for example will reduce the fluoride vapor pressure and, hence emissions, by about 90 percent. This method of control would have to apply to the entire pond which would effectively result in requiring control of existing sources in order to obtain PSD approval for a new source or, it would require a separate cooling pond/gypsum stack for the proposed expansions. The latter is a physical impossibility at New Wales.

Liming, to be effective, also requires a two-pond system; one pond for gypsum sluicing water, and one for process water cooling. Separating the ponds at New Wales would be virtually impossible because of the existing configuration and the limited space for ponds and gypsum stacks.

Assuming it was feasible to separate the ponds and lime the cooling pond, fluoride emissions would still result from gypsum stack and the sluice water pond.

The lime requirements (CaO) for treatment of the pond water can be considered in two parts; that required to raise the pH of all of the water presently in the pond and that required to neutralize the process water during normal plant operation.

It has been reported(2) that 0.157 pounds $Ca(OH)_2$ is required to raise the pH of a gallon of typical pond water to 3.9 and 178 pounds of $Ca(OH)_2$ is required on a steady state basis for each ton of P_2O_5 processed. The New Wales pond system contains 2.4×10^9 gallons of water and the P_2O_5 production rate, proposed after expansion, is 4500 tons per day.

If it is assumed that the initial pond water neutralization would take place over a 90-day period. The initial lime requirement as $Ca(OH)_2$ would be 2493 tons per day [$2.4 \times 10^9 \times 0.157/(2000 \times 90) + 400$]. Steady state liming would require 400 tons per day of $Ca(OH)_2$. Considering the magnitude of the operation, New Wales would probably purchase the lime required for the initial liming and install a calciner and slaker to produce the $Ca(OH)_2$ required for the steady state liming.

Using published EPA emission factors for bulk materials handling, lime production and fuel oil combustion an analysis of the emission burden of such an operation has been estimated. The summary of this analysis is presented in Table 1. In addition to the impact on air quality resulting from the emissions presented in Table 1, the calcining of the lime will require the consumption of 8400 gallons per day of fuel oil(2).

The 660 pounds per day of particulate matter, 3260 pounds per day SO_2, 170 pounds per day NO_x and the fuel oil consumed will result from actions taken to eliminate approximately 540 pounds per day or 100 tons per year of fluorides; fluorides which have been shown not to have an adverse environmental impact.

The other methods of reducing fluoride emissions which have been reported(2) have likewise been shown to be not cost/effective or workable. The transport of gypsum by conveyors rather than by sluicing would be effective only if the cooling pond was limed and liming has been shown to be counter-productive.

In summary, it can be said that the emission of fluorides from the cooling pond/gypsum stack at New Wales will have a severity of 0.11 at the nearest property line. In other studies, pond and chemical complex fluoride emissions have been shown not to create adverse environmental effects. Attempts to control fluoride emissions from pond/stack systems will, in all likelihood, result in the emission of particulate matter, sulfur dioxide and nitrogen oxides that will more than offset the reduction in fluoride emissions sought.

TABLE 1

SUMMARY OF EMISSION BURDEN(1) RESULTING FROM COOLING POND LIMING AT THE RATE OF 400 TPD

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

Activity(3)	Particulate Matter		SO_2		NO_x	
	Potential (lb/day)	Actual (lb/day)	Potential (lb/day)	Actual (lb/day)	Potential (lb/day)	Actual (lb/day)
Receiving	400	100	-	-	-	-
Storage	200	100	-	-	-	-
Crushing and Calcining	22,100	440	3,260	3,260	170	170
Slaking	150	440	-	-	-	-
TOTAL		660		3,260		170

(1) Emission factor from AP-42 and from Technical Guidance for Control of Industrial Process Fugitive Particulate Emission, USEPA, EPA-450/3-77-010, March 1977.

(2) As $Ca(OH)_2$.

(3) Activities include transfer.

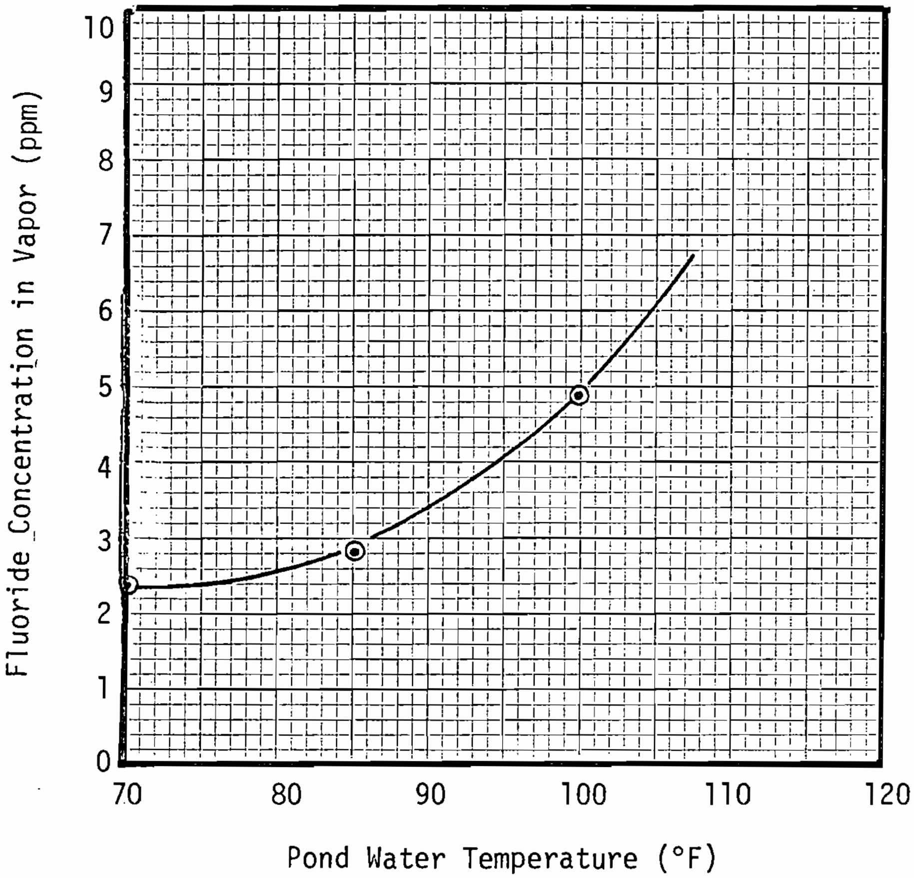

FIGURE 1

FLUORIDE CONCENTRATION RESULTING FROM
FLUORIDE VAPOR PRESSURE EQUILIBRIUM OVER POND WATER(4)

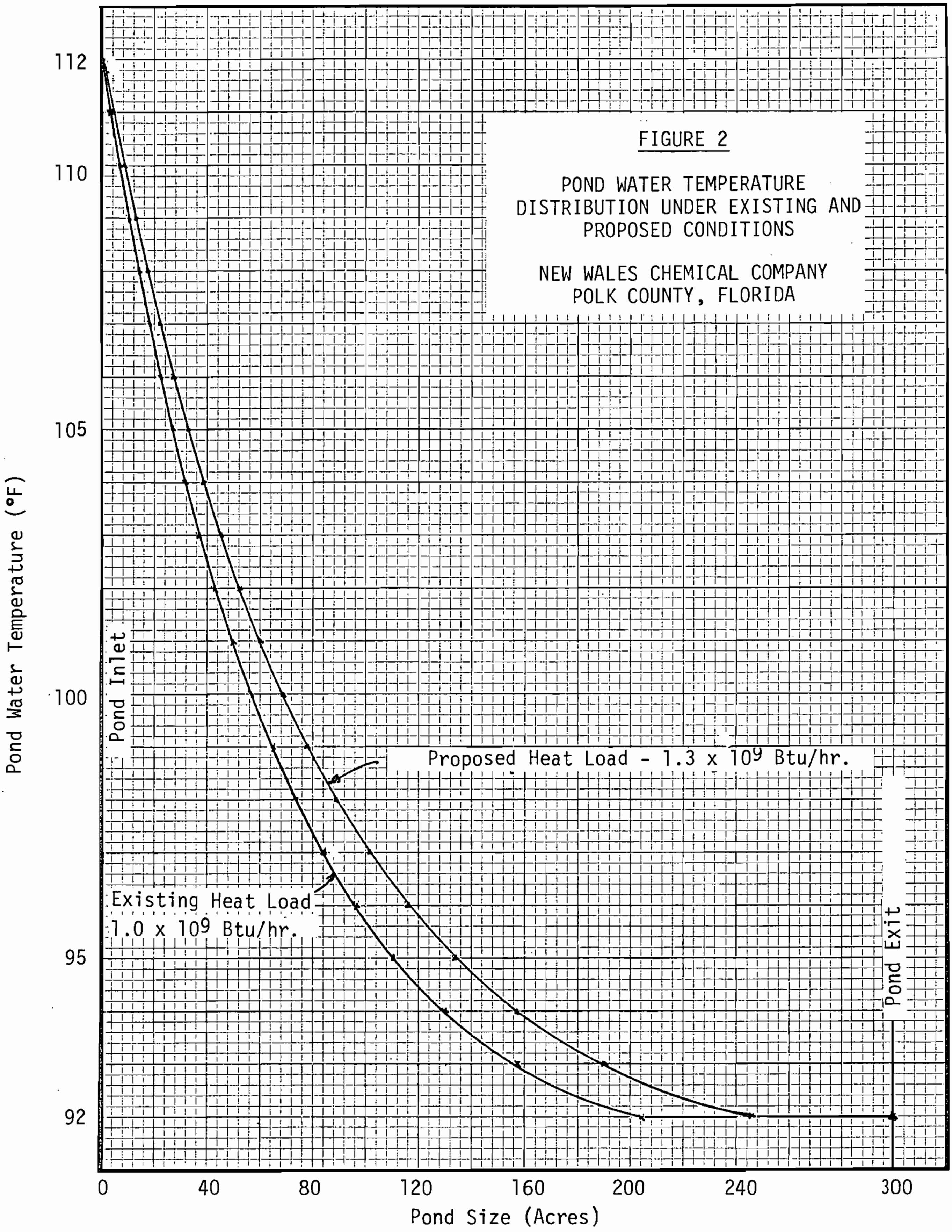

FIGURE 2

POND WATER TEMPERATURE DISTRIBUTION UNDER EXISTING AND PROPOSED CONDITIONS

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

(3)

(4)

O means mon. sites SO2

1 mi to site #2 from N.W.

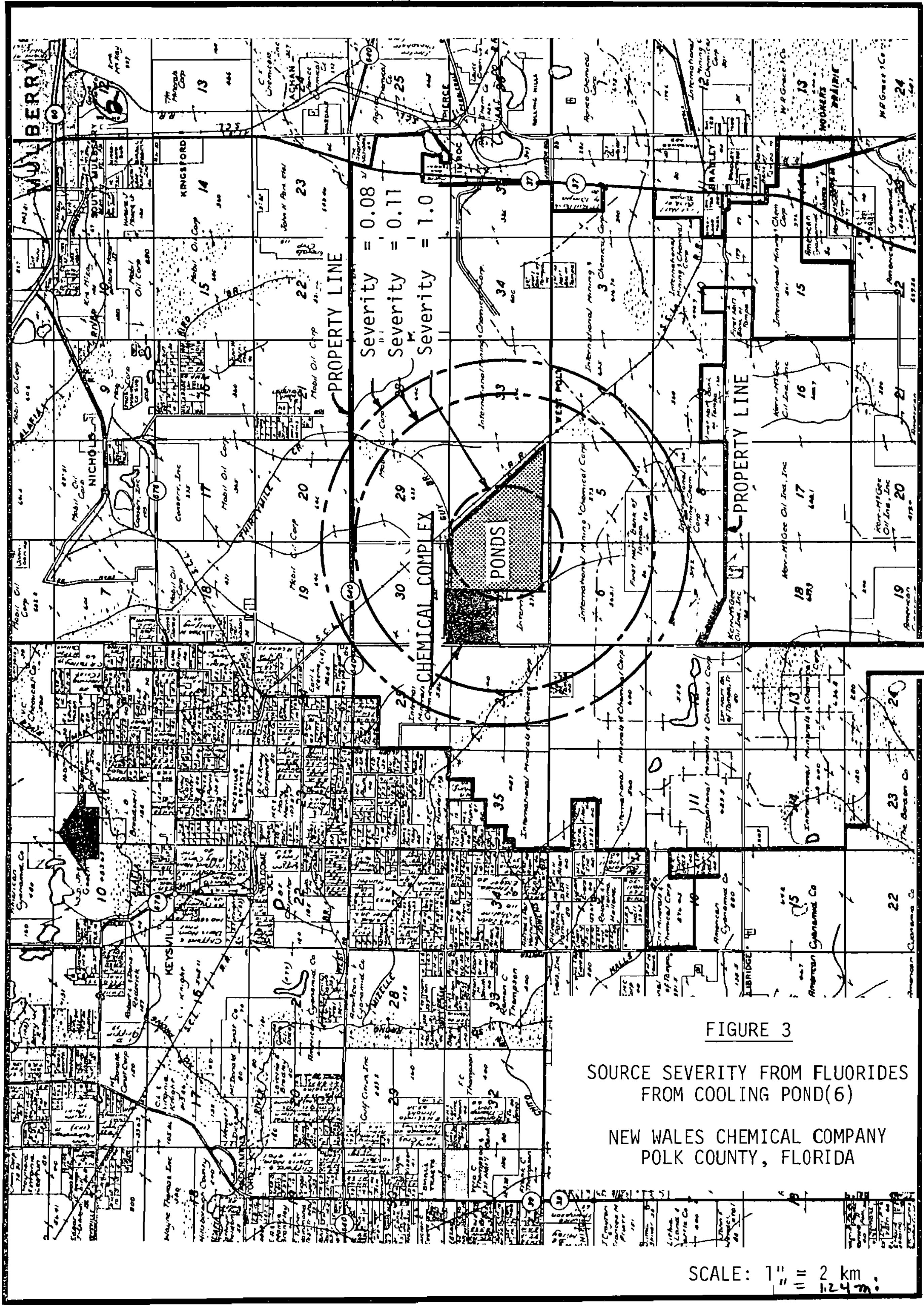

FIGURE 3

SOURCE SEVERITY FROM FLUORIDES FROM COOLING POND(6)

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

SCALE: 1" = 2 km
" = 1.24 mi.

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SECTION 1

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ATTACHMENT 1

FLUORINE CHEMICAL REDISTRIBUTION IN RELATION TO GYPSUM STORAGE POND SYSTEMS

by

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I. Introduction

1. In general, there are three major considerations of environmental significance with regard to fluorine chemical distribution and containment in gypsum storage pond systems.

The primary consideration quite obviously concerns civil engineering design to ensure mechanical integrity and performance of the containment structure for waste byproduct and process water storage.

In more recent years the emphasis has been extended to process engineering considerations of water management and recycle uses in the total manufacturing process, which has markedly affected the chemical redistribution of fluoride within the storage pond system.

The third fundamental aspect concerns the actual chemical processes that control fluorine behavior throughout the total manufacturing process. Despite its inherent significance and interrelationship to functions of the waste-containment structure and water management practices, the chemistry of fluoride distribution among products and waste streams has been generally neglected and remains poorly defined.

2. Although presently handicapped by this shortcoming in chemical knowledge, it must be recognized that the chemistry of fluorine behavior is fundamental to virtually all aspects of environmental controls in waste management—especially so in any rational approach to realistic, attainable waste control procedures. The governing chemical laws in this phosphate chemical processing system, however poorly defined at present, cannot be legislated, repealed, or ignored.

3. The objective of this report is to assemble and outline a qualitative chemical model of fluoride distribution in the total manufacturing process as it relates to the storage pond system. Its purpose is to establish the scope of the problem based on present knowledge of the chemical subsystems and to identify areas where further research is needed to guide responsible environmental actions.

Fluorine transport to the storage pond system follows two basic pathways; namely, fluoride delivered from the acidulation process as byproduct wastes consigned to the gypsum storage section and fluoride recovered in recycled process water uses and returned to the pond water storage section where comingling of aqueous effluents occurs.

II. Interrelation of Pond System to the Total Process

To provide a frame of reference, the interrelationships of the storage pond system to the total phosphate manufacturing process are diagrammed in Figure 1 showing the two primary inflows of fluoride to the storage pond system.

4. (A) Past Commercial Practices

Up until quite recently the phosphate industry had operated on high-quality, premium-grade phosphate raw materials. Similar dihydrate acidulation processes were employed with gypsum pond systems serving an end-of-the-line disposal function. These combined effects not only simplified the fluoride chemical redistribution model but also led to similar chemical traits among storage pond systems. Compositions of pond waters were more highly uniform, and industry-wide approximations of cake composition as well as tonnage ratios of cake production, process water (PW) consumption, and stacking water losses in terms of P_2O_5 feed capacity were reasonable engineering estimates.

5. (B) Present and Future Trends

These conditions no longer hold true in current operations. There has been a progressive slippage in the grade and chemical composition of phosphate raw materials, coupled with divergence in acidulation processes and plant operating practices. Furthermore, the disposal pond system has been integrated into the total manufacturing operation so as to perform a kidney-like function for waste streams and process water.

This combination of current practices contributes to divergent and more complex fluoride chemical redistribution models. Future prospects are that the fluoride distribution patterns will undergo progressive change on an individual industry basis.

6. (C) Outlook

As a consequence, the chemistry of fluoride in the storage pond system as well as in upstream processing stages of rock and wet-process acid no longer can be satisfactorily described by simplistic reaction models of the past, nor is it valid to view storage pond systems as an isolated, detached terminal stage in the manufacturing operation in making environmental assessments of fluorine distribution.

Unless properly recognized and researched, there is the inherent risk that environmental assessments, particularly remedial actions for fluoride containment, will be fatally flawed by false chemical assumptions.

III. Chemical Redistribution of Fluoride in Acidulation Process Stages

7. The quantity, physical nature, and chemical form of fluoride entering the storage pond system as direct byproducts from the acidulation process involve three interrelated factors. These factors are (1) composition of feed rock, (2) chemical behavior of dissolved fluoride in the digester stage, and (3) the wash-processing and slurry transport of byproduct cake.

8. (A) Variable F-Content of Phosphate Rock Feed

The phosphate-bearing apatite mineral component of domestic commercial phosphate raw materials can be represented by the compositional series of carbonate-substituted francolite-type apatites illustrated in Table I. In this compositional series the relative quantities of F, Na, and Mg increase and the P-content decreases with increasing degree of carbonate substitution, whereas calcium content remains relatively constant due to a compensating decrease in molecular weight. A convenient statistical model (Table I) has been developed to derive apatite compositions from crystallographic unit-cell dimensions determined by precision x-ray powder diffraction analysis.[1,2]

9. Parameters of Phosphate Rock Feed: Representative apatite compositions from domestic commercial deposit sources are compared in Table II which illustrates the range of chemical variability with respect to fluorine content as well as associated constituent elements. Although omitted from discussion here, additional amounts of these and other metal constituents contributed by accessory minerals also influence the chemical model of storage pond systems as described later.

10. The most significant parameters in terms of P_2O_5 production relate to the variable tonnage ratios of fluorine and calcium relative to P_2O_5 as a function of apatite composition. For a given feed-rock grade the quantities of input fluorine, byproduct gypsum produced, and total cake solids can differ significantly (Table II). Corresponding changes also occur in process water consumed as hydrate water and in stacking loss. For different feed-rock grades these parameter values will change in predictable manner.

Each parameter exerts influence, however subtle, on the total fluorine distribution pattern. The approximations of these terms used by industry suffice for engineering estimates of materials balances but are inadequate to precisely define fluorine balances.

11. (B) Fluorine Redistribution in the Acidulation Stage

Current fundamental knowledge of fluoride chemical behavior in the digester stage, especially with today's lower quality feed rocks, mainly permits only a qualitative modeling of the chemical redistribution process among product and waste streams.

Controlling Variables: Based on extensive laboratory research and supporting observations from pilot-plant studies and actual commercial samples, the controlling compositional variables of the wet-process acid intermediate product are those summarized in Table III.[3]

Precipitation of fluoride dissolved from the rock is governed primarily by the interacting concentration levels of Al, Si, Na, Mg, Ca, and F released into solution from the feed rock mineral mixture.

The quantities of these controlling chemical constituents, as for example in a typical central Florida rock, vary over a considerable range. However, the actual concentrations in the WPA intermediate depend on the individual solubility properties of the contributing mineral components.

12. Modes of Fluoride Precipitation: Twelve modes of F^- precipitation have been identified in laboratory research based on the illustrated range of rock compositions for central Florida raw materials; compositions of these 12 fluoride precipitates are shown in Table IV. Additional modes undoubtedly exist for raw material sources falling outside this selected range, as for example the North Carolina and western U.S. deposit types.

Nine of these twelve precipitation processes have been recognized from time to time in commercial production due to unmonitored fluctuations in the concentrations of controlling metal constituents caused by subtle changes in rock mineralogy.

13. Quantity of Fluorine Removed by Precipitation: In the past when premium-quality raw materials were mainly used by industry, the singular or predominate fluoride salt component in byproduct gypsum cake was Na_2SiF_6 and generally accounted for about 20 to 30% of the input fluorine.[4]

With increasing frequency based on today's raw materials, other fluoride salts are being observed to coprecipitate with or substantially replace this traditional Na_2SiF_6 composition. As a result the quantity of input fluorine transferred from the WPA intermediate to byproduct cake solids through precipitation varies over much wider limits according to the individual solubility properties of the twelve possible fluoride salts.[3]

Precipitation of the more soluble $NaKSiF_6$ composition decreases the amount of fluoride transferred to the cake solids in comparison to Na_2SiF_6. However, precipitation of either ralstonite or chukhrovite in place of alkali fluosilicate compositions greatly increases the percentage of input fluorine reporting to byproduct cake (see Table IV).

Aside from fluoride, the storage pond chemical system is also affected by the metal constituents selectively removed by fluoride precipitation and transferred to the pond either in a solid or redissolved state.

14. (C) Fluoride Redistribution During Cake Processing

Solubility Behavior: The initial distribution of input fluorine between acid product and fresh byproduct cake is controlled by the respective saturation limits of the individual fluoride salts in the WPA liquid phase (nominally about 30% P_2O_5; 1.5 to 2.5% SO_3). These solubility limits are compared in Table V and reveal a 40-fold difference between the least soluble and most soluble salt compositions.

After removal by filtration, however, the individual fluoride salts differ markedly in their relative stabilities during cake washing and slurry transport in contact with these more dilute aqueous solutions used to process and transport cake solids, as shown by the solubility data in Table V.

Some fluoride may be recycled to the product stream during cake washing by partial stripping of the more highly soluble fluoride salts, if present. Further chemical erosion of the fluoride salts can occur during slurry transport leading to a new fluoride distribution ratio between cake solids and the suspending pond solution as discharged to the waste storage system.

15. Behavior of Fluoaluminates and Fluosilicates: Alkaline-earth fluosilicates are the least resistant to these aqueous treatments and constitute unstable solid components as recovered from the WPA intermediate in the byproduct cake. Although less soluble, the alkali fluoaluminates and fluosilicates show a similar tendency to be stripped by the contacting aqueous solution.

As an illustration, Figure 2 compares the relative solubilities of the three alkali fluosilicate salts in the WPA liquid product, typical pond water solution, and distilled water. The greatly increased solubility of sodium fluosilicate compositions--especially $NaKSiF_6$--in the dilute acidic pond water solvent accounts for their ready tendency to be stripped from cake solids from the early stages of cake washing onward.

16. Fluoride Salt Alteration Processes: The dissolution or alterations of fluoride salts which are initiated during washing and slurry transport continue after discharge into the storage pond. The nature of these individual alteration processes is described in Table VI. A characteristic feature of the overall decomposition process is a reprecipitation of fluoride in the pond system by dissolved calcium in the form of highly insoluble salts, principally chukhrovite and CaF_2. The original metal cations that transported fluoride from WPA to cake solids largely report to the pond solution where they tend to accumulate and get recycled.

IV. The Storage Pond Chemical System

17. (A) General Functional Features

The principal structural features[5] and functions of present-day industrial storage pond systems are illustrated in Figure 3. Although they embody similar water management schemes and design engineering features of compartmented functions, the individual ponds are not necessarily comparable chemical systems. Dissimilarities arise from two basic sources.

As previously discussed, the compositions of inflowing waste streams from the rock acidulation stages will differ in quantity and form of fluoride as well as associated impurity metals, depending on both the particular raw material feed and the proprietary conditions of intermediate process stages.

18. Further chemical disturbances of the storage pond system arise from various recycled uses of stored pond water as required for a particular manufacturing plant operation. Collectively these recycle streams return additional fluoride along with silica, phosphate, and possible ammonia to the storage pond system. The actual quantity of fluoride returned in this manner differs for each industry and will depend on the volume of recycle PW required to operate and its particular functional uses in the manufacturing stages. In addition, fugitive seepage water intercepted by collection ditches and returned to the pond differ in volume and composition for each pond structure.

19. (B) Compositional Uniformity of Pond Water

Despite these aforementioned compositional disturbances from the various inflowing sources of fluoride-bearing liquid and solid streams, individual storage pond systems tend to display a long-term compositional uniformity aside from weather-related concentration or dilution effects. This is a unique comparative feature of most storage pond systems in that they tend to maintain a steady-state balance notably with regard to fluoride and P_2O_5 concentration levels as well as pH.

The concentration levels of the principal dissolved constituents do vary, however, among storage pond water systems, but not widely so. Listed in Table VII are the approximate concentration ranges for dissolved constituents based on a representative sampling of Florida-based storage systems.[6]

Since no net accumulation of fluoride appears to occur in the pond aqueous phase, other parts of the total processing system must function as net accumulators for the continuous inflow of fluoride from the various process and recycle streams. Berry and Busot[7] have developed statistical models to account for this quasi-equilibrium condition in the pond water phase and systematically evaluated the effects of operational changes in recycle water usage on pond water composition.

20. (C) Accountable-Fluorine Distribution Balances

Environmental considerations of fluoride redistribution processes in storage pond systems with regard to the magnitude and pathways of fluoride losses have been a subject of wide controversy and speculation.

This problem of environmental accountability can be reduced to proper perspective by accessing the fluorine balance within a total manufacturing system that can be reasonably defined and analyzed.

The total fluoride balance can be expressed as

$$F_{input} = C_{pw} + F_p + F_w + F_e$$

On a time-averaged basis, the F_{input} from raw material feed must ultimately be accounted for either in manufactured products (F_p), waste products (F_w) (either liquid or solid), or in the collective environmental losses (F_e) arising from volatile emission, pond overflow, and subterranian seepage. Since pond water compositions (C_{pw}) generally show no progressive net accumulation of dissolved fluoride, this term can be eliminated as a constant in the above balance. Thus the terms F_{input}, F_p, and F_w can be evaluated on the basis of established chemical principles, defined process parameters, product balances, and chemically defined compositions of products and byproducts. Concerning the latter, the precision of this modeling could be substantially improved by more refined compositional data in those instances where only spot analyses rather than composite data were available.

21. Calculated Distribution Models: Using this distribution model, accountable fluorine balances were constructed for a representative cross section of active industrial storage pond systems. These calculated F-balances for four industrial storage pond systems have been normalized to a 1000 tpd production base for ease of comparison and to protect the data sources.

The selected parameters used as a calculation basis are listed in Table VIII and are based on (1) refined compositional data for raw materials, (2) pertinent tonnage production statistics, (3) refined operating parameters, and (4) the best available in-house analytical descriptions of process streams--usually six-month or yearly composite data. No major assumptions were employed. Since the precision of these calculated F-balances would be improved substantially by more precise analyses of products and waste streams, the computed balances represent first approximations only. However, they establish an order of magnitude to bring the problem of fugitive fluoride losses into proper perspective.

The summarized fluoride distribution balances for four industry sources are shown in Table IX. Net unaccountable fluoride balances range from 0 to only 3.5%. Although only approximations, their significance rests in removing inflated speculations concerning the order of magnitude of fugitive losses. Considering the combined acreage of these four storage systems (> 1000 acres) exposed to the environment and their aggregate amount of unaccountable fluoride, there is no clear indication that catastrophic losses are occurring by subterranian seepage and volatile emission.

V. Fluoride Chemical Equilibria in Storage Pond Systems

22. Environmental considerations of fluoride distribution or transport in storage pond systems must take into account a set of complex interrelated chemical equilibration processes. These competing equilibration processes, as illustrated in Figure 4, govern the chemical state of fluorine and its distribution in the pond system.

23. (A) Pond Solution Phase

Pond water compositions characteristically include a number of dissolved metal constituents that are capable of reacting with (F^-) to form stable soluble complex ions over the ranges of pH and concentration levels normally found.

While the available reference data clearly indicate that the $HF-H_2SiF_6$ equilibrium reaction primarily controls volatile fluoride emissions, other equilibrium reactions compete for dissolved (F^-) to produce stable, nonvolatile complex ions.[8] Some important examples are given in Table X. Complexes formed by dissolved Al^{3+}, either alone or as the phosphate ligand, tend to be especially stable complexes.

As a consequence, the concentration of total fluorine in pond water solution as determined by conventional chemical analysis and by the fluoride-ion specific electrode method may show significant deviation, since some dissolved fluoride can occur in species other than HF_{aq} and (F^-). For this reason, it may be inappropriate to evaluate the $HF-H_2SiF_6$ equilibrium distribution on the basis of "total fluorine" concentration in the pond water, unless these other compositional disturbances have been properly evaluated.

24. (B) Pond Solid Phase

The pond solid and liquid phases interact according to two opposing equilibration processes that affect the net concentration of dissolved (F^-), as shown in Table XI.

Fluoride is continuously removed from the pond solution by coprecipitation with calcium to form CaF_2 and chukhrovite. Laboratory studies indicate these precipitations to be the principal long-term immobilization processes. With increasing concentration of dissolved Mg^{2+} in pond water, either ralstonite or MgF_2 appears as secondary precipitating solid phases.

25. The opposing group of equilibration processes represents the progressive elimination of the more soluble fluoride compositions in freshly discharged slurry solids. Solubility characteristics of the controlling fluoride solid phases determine the recycle rate of fluoride to the pond water phase. Fluoride salts containing calcium undergo incongruent dissolution, releasing only part of their fluoride to the aqueous solution as illustrated by the last two entries in Table XI.

Decomposition of the more soluble fluoride salts, which usually begins during cake washing and slurry transport, represents short-term equilibration processes confined mainly to the uppermost layer of freshly deposited cake solids.

However, the principal long-term reversion processes involving precipitation of CaF_2 and chukhrovite most likely occur throughout the cake mass in contact with stacking water and percolating pond water. The highly insoluble nature of both reversion products would tend to immobilize soluble fluoride within the confines of the storage containment system.

26. (C) Pond Vapor Phase

The transport of fluoride from pond water to the vapor phase is quite obviously one of the principal environmental concerns. Some of the past difficulties in chemical modeling of the emission process were due to oversimplistic assumptions and inadequate data. It is clearly evident from the previous discussion of equilibration processes that the interacting chemical systems which control fluorine distribution are complex and presently definable largely in a qualitative sense.

As cited earlier in the discussion of pond water chemistry (Table X), the most probable equilibrium reaction controlling vapor-phase emission concerns the ionization of molecular HF_{aq} and its interaction with SiO_{2aq} to establish an equilibrium concentration of H_2SiF_6 dissociation products in solution.

Assuming that SiO_2 is not a limiting constituent to establishing equilibrium, i.e., the mole ratio $F/SiO_2 \leq 6$, the available data on this equilibrium model can be tested by Henry's Law for consistency and also to predict the net transport of fluoride to the vapor.

The overall reaction (in solution) can be expressed as

$$6HF + SiO_2 \rightleftarrows H_2SiF_6 + 2H_2O$$

where Henry's Law states

$$P_{Fv} = K \bullet C_{Fs} \text{ or } P_{Fv} = 1.58 \times 10^{-7}(C_{ppm})$$

in which

P_{Fv} = pressure (mmHg°) of total F in vapor phase

C_{Fs} = concentration (moles/liter) F in solution

C_{ppm} = concentration (ppm) F in solution

K = proportionality constant

27. Vapor Pressure of Total F: The most comprehensive data pertinent to pond systems are Tatera's studies[9] of the H_2SiF_6-H_2O and H_2SiF_6-pond water systems, Smirnova's study[10] of the H_2SiF_6-H_2O system with and without an added H_3PO_4 component, and earlier studies by Baur[11] of the HF-H_2SiF_6-H_2O system.

As shown by the Henry's Law plot of data in Figure 5, there is a high correlation among the data sources ($R^2 = 0.95$) relating the vapor pressure of fluoride components (total F) to fluoride concentration of the aqueous phase. For example, a PW concentration of 10,000 ppm (or 0.53 moles/liter) would yield a vapor pressure for total F $\simeq 1.6 \times 10^{-3}$ mmHg°, which corresponds roughly to about 0.5 milligrams F per cubic meter.

28. Composition of Vapor Phase: The composition of fluoride species in the total F vapor phase has been investigated by both Smirnova and Baur using different approaches. Baur computed the molar proportions of HF and SiF_4 based on their respective partial pressure contributions to the measured total pressure. Smirnova evaluated this mole ratio by actual chemical analysis of the vapor phase products.

As illustrated in Figure 6, a semi-log plot of both sets of data shows close agreement and predicts an increasing predominance of HF over SiF_4 in the vapor phase with decreasing concentration of F in solution. The HF/SiF_4 mole ratio value is roughly proportional to 1/% F, or about 100:1 for a pond water concentration of 10,000 ppm F.

The series of interdependent equilibrium reactions that control the relative concentrations of possible molecular species contributing to vapor emission are described in Table XII. Consideration of their rate constants suggests the most probable molecular species available for transport to the vapor phase and supports the predicted high mole ratio value of HF/SiF_4 derived from the experimental data.

Among the possible molecular forms, HF is the most abundant stable species because of its very small ionization constant[12] ($K = 10^{-3.2}$ at 25°C, corresponding to about 2% dissociation at a pond water pH of 1.5). Thus, the dominant equilibration between the solution and vapor phases is most likely to be molecular $HF_{aq} \rightleftarrows HF_g$.

Molecular H_2SiF_6, however, has not been established to exist in the vapor state, nor is it likely to persist in solution in significant concentration because of its infinitely large dissociation constant (equation III, Table XII).

Similarly, the concentration of molecular SiF_4 produced by the dissociation of H_2SiF_6 (equations IV and V, Table XII) will remain small due to its vigorous decomposition reaction with free water. This precludes any significant buildup of molecular SiF_4 in the highly dilute pond water phase and it also would lead to high instability in contact with moist atmosphere upon volatilization, according to equation IV, Table XII.

Thus, the overall reaction sequence appears to favor evolution of fluorine predominately as molecular HF from the highly dilute pond water compositions (nominally 0.5 to 1.0% F), with concomitant removal of SiO_2 from solution by precipitation as the equilibrium shifts to maintain the concentration of undissociated HF_{aq} in solution. Except for Tatera's studies, most of the literature examples deal with higher fluoride concentrations than found in gypsum pond systems. As shown by Figure 6, quite obviously the SiF_4 content of the vapor phase would increase significantly at an exponential rate with a progressive increase in (F^-) in solution. This is the probable source of speculation that SiF_4 is a major component of pond emissions to the atmosphere.

29. Effect of Silica on F-Emission: In this foregoing discussion, silica concentration was not a limiting or rate-determining factor, but all pond systems do not necessarily satisfy this criterion.

According to the SiO_2-promoted back reactions listed in Table XIII, the addition of silica to decrease the F/SiO_2 mole ratio should reduce the concentration of molecular HF, which mainly contributes to F emission.

Smirnova's data based on limited tests appear to demonstrate this principle. As shown in Table XIII, total F emission decreased sharply with a progressive reduction in the F/SiO_2 mole ratio (in solution). A comparison of Smirnova's test ratios with actual values from three different pond systems clearly suggests that F emission rates may differ markedly for ponds having similar fluoride concentrations but different levels of dissolved or active silica.

Summarizing the currently available data, tentative relationships exist to predict the quantity and molecular form of fluoride transported to the vapor phase in relation to pond water concentration effects. However, the concentration terms of both (F^-) and dissolved SiO_2 must be considered in these projections of fluoride emission--not just "total F" alone.

VI. Chemistry of F-Removal From Pond Overflow and Seepage

The two final considerations regarding fluoride distribution concern fluoride removal during controlled discharge of excess pond water and the fate of fluoride in fugitive subterranian seepage losses.

30. (A) Chemistry of Lime-Treated Pond Discharge

Lime treatment (either limestone or hydrated lime) has been widely used to reduce the content of dissolved fluoride (and P_2O_5) in various industrial and municipal wastes with varying degrees of success. Difficulties arise from attaining the desired terminal concentration levels of F^- and PO_4^{3-} in treated waste water effluents using projections based on the generally assumed pure chemical phase systems.[13,14,15]

Any proposed adoption of the single or multi-stage lime treatment of gypsum pond effluent water will require careful reappraisal of these assumed chemical models. There is ample evidence in the literature[15,16,17,18] to show that the very low equilibrium concentrations of F^- and P_2O_5 found in the pure systems can be markedly increased by introducing small concentrations of anionic impurities (CO_3^{2-}, SO_4^{2-}, Cl^-) or metal cations (Mg^{2+}) into these systems. The physical chemical changes in these expanded phase systems responsible for altered concentration effect involve displacements of stability fields and solubility isotherms in the phase system as well as ion complexing[16,18] which are beyond the scope of this report. Nevertheless, these physical chemical constraints apply to impure pond water compositions so that the lowest obtainable concentration limits of (F^-) and (PO_4^{3-}) may differ sharply from laboratory model systems or analogies with other lime-treated industrial or municipal effluents.

31. Precipitation Models of Lime Treatment: Very little published literature exists on the actual performance of the model phase systems under the conditions of chemical adulteration found in storage pond water systems. Some unpublished data from in-house testing (personal communications) show displaced maxima in (F^-) and (PO_4^{3-}) removal by lime precipitation in contrast to phase model predictions.

be exceedingly slow in the range of 10^{-5} to 10^{-9} cm/sec. Also, in the case of the central-south Florida production region, the stratigraphic sequence and composition of sediments down to the principal aquifer in the Hawthorn Formation are well described,[19,20,21] showing abundant clays and carbonates in discrete beds as well as dispersed throughout the alluvial sediments. By inference to several decades of research on fertilizer-soil mineral reaction chemistry,[22,23] it is well established that anionic constituents such as (PO_4^{3-}), (SO_4^{2-}), and (F^-) react rapidly with clays, and especially carbonate mineral components, in soils to become immobilized as highly insoluble reaction products.

The above circumstances suggest low-volume seepage rates to subterranian sediments, with abundant sources of reactive soil mineral components to intercept and immobilize anionic contaminants well in advance of penetration to the regional aquifer zone. These relationships await quantitative verification.

In isolated cases where details of the precipitation mechanisms were identified through precise solid-phase characterizations (unpublished TVA data), the phase chemistry within the pH range of interest (3-9) was found to deviate markedly from the predicted thermodynamic model systems. These comparisons are summarized in Figure 7.

As shown by the diagrammed precipitation processes, phosphate removal is usually governed by octacalcium phosphate (OCP) precipitation over an extended range of metastability. Because of OCP's much higher solubility in comparison to apatitic phosphate ($K_{OCP} = 10^{-49}$ versus $K_{AP} = 10^{-119}$), higher residual concentration levels of P_2O_5 in solution are to be expected, especially in the acidic pH range. The presence of soluble Mg^{2+} in concentrations as low as 200 ppm stabilizes OCP against hydrolysis to the stable apatite phase in the basic pH range so that high P_2O_5 concentrations well above projected limits of 30 to 35 ppm may persist in the second liming stage.

32. Regarding (F^-) removal, the unpredicted substantial removal of fluoride in the acidic range of first-stage liming usually has been traced to precipitation of chukhrovite, $Ca_4AlF_6SiF_6(F,OH)SO_4 \cdot 10H_2O$, rather than fluorapatite or CaF_2 compositions. Quite obviously, the efficiency of F-removal by this mechanism depends on concentration levels of coprecipitating metal constituents aside from calcium. If first-stage precipitates containing chukhrovite are carried into the second-stage liming, this complex fluoride decomposes incongruently above pH 7, releasing some fluoride to solution and reprecipitating the remainder as CaF_2.

In summary, the two-stage liming treatment of pond water discharge has obvious merit as the cheapest, best available method to reduce (F^-) and (PO_4^{3-}) concentration levels and adjust pH. However, our present chemical knowledge provides no rational basis for selecting set values of concentration limits, however desirable.

33. (B) Chemical Modeling of Subterranian Seepage

Although the magnitude of subterranian seepage and the potential migration of dissolved fluoride and phosphate into aquifers is a major environmental concern, virtually no published accounts are available that quantify these distribution patterns. It constitutes, therefore, one of the most poorly resolved facets of fluoride distribution in storage pond systems.

Some information about controlling parameters is available, however. Data on percolation rates through compacted aged gypsum cake and the underlying clayed sediments have been reported by Wissa[5] to

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TABLE I

THE APATITE COMPONENT OF PHOSPHATE RAW MATERIALS

Composition Series

$$Ca_{10}(PO_4)_6F_2 \text{ — } Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}(F,OH)_2$$

(fluorapatite) (francolite)

Composition Range

Constituent (%)	Fluorapatite (x = 0)	Francolite (x/6-x = 0.30)[a]
CaO	55.65	55.13
P_2O_5	42.21	34.07
CO_2	0	6.34
F	3.77	5.04
Na_2O	0	1.28
MgO	0	0.65

[a] Corresponds to upper substitution limit ($\underline{a}_\circ$ = 9.313Å).

X-ray Composition Models

$$\text{Unit-cell } \underline{a}_\circ \text{ Å (obs.)} = 9.374 - 0.204\ (x/6-x)$$

$$(Na)_a = 1.327\ (x/6-x)$$

$$(Mg)_b = 0.515\ (x/6-x)$$

TABLE II

PARAMETERS OF APATITE COMPOSITION AFFECTING FLUORIDE BALANCES

Apatite Composition

		Theor. composition, wt. %					
Source	Mean a_o (XR)	CaO	P_2O_5	F	CO_2	Na_2O	MgO
Western U.S.	9.357	55.54	39.60	4.18	2.05	0.35	0.17
C. Florida	9.341	55.43	37.40	4.52	3.75	0.69	0.35
S. Florida	9.334	55.36	36.52	4.67	4.44	0.82	0.41
N. Florida	9.332	55.34	36.28	4.70	4.62	0.86	0.43
N,S Carolina	9.323	55.23	35.20	4.87	5.46	1.05	0.55

Parameters

			68 BPL feed			
Source	CaO/P_2O_5	F/P_2O_5	% apatite	% F	% CaO	t cake: t P_2O_5[a]
Western U.S.	1.403	0.106	78.6	3.29	43.65	5.00
C. Florida	1.482	0.121	83.2	3.76	46.12	5.09
S. Florida	1.516	0.128	85.2	3.98	47.17	5.14
N. Florida	1.525	0.130	85.8	4.03	47.48	5.15
N,S Carolina	1.569	0.138	88.4	4.31	48.82	5.20

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[a] Gypsum plus inerts; does not include F-salt component, which would increase ratio by about 0.05, assuming 25% of input F removed as Na_2SiF_6.

TABLE III

PARAMETERS OF F DISTRIBUTION IN DIGESTER STAGE

Controlling dissolved components

Al^{3+}, Si^{4+}, Na^{+}, Mg^{2+}, F^{-}, (Ca)

Sources

Apatite:	Na	Mg	F	
Accessories:	Na	Mg	Al	Si

Variability (C.F. 70 BPL)

	Mean wt. %	Obs. range
Na_2O	0.60	0.28-0.82
MgO	0.30	0.15-0.52
Al_2O_3	1.07	0.30-1.42
SiO_2	4.69	2.50-7.40
F	3.78	3.60-3.90

Solubility in F.G. WPA

Apatite source:	~ 100%
Accessory source:	Highly variable

TABLE IV

POSSIBLE MODES OF F PRECIPITATION IN F.G. WPA SOLUTION

Fluosilicates	Fluoaluminates
Na_2SiF_6	Na_3AlF_6
$NaKSiF_6$	Na_2KAlF_6
K_2SiF_6	$Ca_3(AlF_6)_2 \cdot 4H_2O$
$CaSiF_6 \cdot 2H_2O$	$(Mg_xNa_yAl_z)AlF_6 \cdot 2H_2O$
$MgSiF_6 \cdot 6H_2O$	

Simple Fluorides	Complex Fluorides
CaF_2	$Ca_4AlSiSO_4F_{13} \cdot 10H_2O$
MgF_2	

F Distributed to Cake (% of Input)	
Na_2SiF_6	20-30%
$(NaMg)_xAl_{2-x}F_6 \cdot 2H_2O$	$\leq$ 70%
$Ca_4AlSiSO_4F_{13} \cdot 10H_2O$	80-85%

TABLE V

SOLUBILITY PARAMETERS AFFECTING F DISTRIBUTION DURING CAKE WASHING AND SLURRY TRANSPORT

	Solubility (wt. % at 25°C) in			
F-salt	F. G. WPA ($30\%\ P_2O_5$)	Wash water ($5\%\ P_2O_5$)	Slurry water ($1\%\ P_2O_5$)	Dist. H_2O
Na_2SiF_6	0.20	0.87	1.11	0.50
K_2SiF_6	0.25	0.21	0.23	0.14
$NaKSiF_6$	0.26	0.68	1.13	0.72
$CaSiF_6 \cdot 2H_2O$	1.80	23.6	28.8	31.4
$MgSiF_6 \cdot 6H_2O$	4.00	32.8	35.2	36.0
Na_3AlF_6	0.4	0.08	0.51	<0.02
NaK_2AlF_6	0.50	<0.10	0.36	<0.03
$Ca_3(AlF_6)_2 \cdot 4H_2O$	0.2	<0.09	0.36	<0.02
$MgNaAlF_6 \cdot 2H_2O$	0.5	0.07	<0.25	<0.04
$Ca_4SO_4AlSiF_{13} \cdot 10H_2O$	0.2	0.2	<0.01	<0.04
CaF_2	0.1	0.07	<0.01	0.04
MgF_2	0.5	0.23	0.31	<0.02

TABLE VI

F REDISTRIBUTION IN SLURRY DISCHARGE TO POND

F-salt	Solubility in PW (g/ℓ)	Change in liquid composition		Alteration phases	
		Increase	Decrease	Solid	Gas
Na_2SiF_6	9.0	Na,F,Si,SO_3	Ca	CaF_2	
$NaKSiF_6$	12.0	Na,K,F,Si	Ca,SO_3	K_2SiF_6 + CaF_2	
K_2SiF_6	1.7	K,F,Si,SO_3	Ca	CaF_2	
$CaSiF_6 \cdot 2H_2O$	33.0	Ca,F,Si		CaF_2	HF/SiF_4
$MgSiF_6 \cdot 6H_2O$	37.0	Mg,F,Si	Ca,SO_3	$CaSO_4 \cdot 2H_2O$	HF/SiF_4
Na_3AlF_6	5.2	Na,Al,F,SO_3	Ca,Si	CaF_2 + CHK	
Na_2KAlF_6	2.0	Na,K,Al	Ca,SO_3,F	CHK	
$Ca_3(AlF_6)_2 \cdot 4H_2O$	2.5	Al,F	Ca,SO_3	CaF_2 + CHK	
$NaMgAlF_6 \cdot 2H_2O$	2.5	Na,Mg,F,SO_3	Ca,Al	CaF_2	
Chukhrovite	<<0.1		Ca,Al,Si,F,SO_3	CHK	
CaF_2	<<0.1		Ca,SO_3	$CaSO_4 \cdot 2H_2O$	
MgF_2	3.1	Mg,F	Ca,SO_3	CaF_2	

TABLE VII

APPROXIMATE RANGES IN POND WATER COMPOSITION

Constituent	Range (ppm)
F	900 - 11000
P	800 - 9500
SO_3	1850 - 7700
Si	900 - 3120
Al	70 - 265
Ca	360 - 3400
Mg	40 - 362
Na	210 - 2040
K	10 - 190
Fe	80 - 770
NH_3-N	0 - 2200
Cl	55 - 10800

Other Properties

pH: 1.2 - 2.5   P/F = 0.52 - 2.82   MR F/Si: 4.9 - 7.2

TABLE VIII

Parameters of Individual Fluorine Distribution Balances

(Normalized to 1000 tpd P_2O_5 Production)

	Company A	Company B	Company C	Company D
Phosphate Rock Feed[a]				
Wt. ratio $CaO:P_2O_5$	1.49	1.50[b]	1.50	1.48
Wt. ratio $F:P_2O_5$	0.123	0.118[b]	0.118	0.121
BPL	67	67.3[b]	63.4	65.5
Wt. % apatite	82.8	83.9[b]	78.5	80.3
Byproduct Filter Cake				
Gypsum content (tpd)	4578	4593	4593	4547
Wt. ratio total cake:t P_2O_5	5.18	5.17	5.37	5.26
% of input F in cake solids	21.0	26.2	19.6	26.0
Stacked water (% of cake)	30	30	30	30
F (ppm) in stacked PW[c]	9000	3100	5900	6500
PW Losses or Gains				
Stacking H_2O loss (tpd)	2221	2215	2302	2254
Gypsum hydrate H_2O (tpd)	957	961	962	952
H_2O to WPA intermediates (tpd)	1222[d]	1000	1396	240
Tons makeup H_2O:t P_2O_5[e]	4.40	4.18	4.66	4.21
Recycled Seepage ≡ Fresh Water	-	2625[f]	-	-
Allowable F Stack Emission (tons)[g]	0.2	0.2	0.2	0.2

---

[a] Based on company analyses and supplemental TVA data on apatite characterization of the specific rock sources.

[b] Weighted mean of different feed rock compositions used daily in WPA production.

[c] Yearly average of pond water composition (1977 or 1975).

[d] Based on production ratio of WPA grades.

[e] Reported value of 4.6 assumed in earlier modeling (Berry and Busot).

[f] Equivalent tonnage of "fresh water" return, based on reported 75% depletion of F during seepage process.

[g] Maximum emission according to EPA value of 0.4 lb/t P_2O_5 capacity.

TABLE IX

Fluoride Chemical Distribution Balances[a]

(Normalized to 1000 tpd P_2O_5 Production)

	Company A		Company B		Company C		Company D	
	Process material	F content	Process material	F content	Process material	F content	Process material	F conten
Accountable Fluoride								
1. F to waste streams:								
Gypsum cake (total solids)	5182	25.70	5169	31.02	5370	22.55	5261	33.83
Stacked water (PW)	2221	19.99	2215	6.86	2302	13.58	2255	14.65
2. F to byproduct H_2SiF_6	0		22.30	17.64	0		33.59	26.58
3. F to manufactured products:								
WPA (direct sales)	0		376.6[b]	3.20[b]	0		525.5	4.78
GTSP	0		428.6	10.16	2129	50.02	719.1	18.05
DAP	2174	37.50	1142.9	24.11	0		821.9	15.04
4. F uptake by replaced PW[c]	4401	39.61	4176.5	12.95	4659	27.50	(3446)	(22.40)
5. F uptake by recycled seepage	N.A.[e]	N.A.	2625	8.14	N.A.[e]	N.A.	N.A.[e]	N.A.
6. F removed from PW discharge	0		0		0		1235	8.03
7. F as allowed stack emissions[f]		0.162		0.143		0.160		0.149
Total (accountable)		122.96		114.22		113.81		121.1
F Input (Feed Rock)		122.63		118.29		115.51		120.8
Net F (unaccountable)		(-0.33)		+4.07		+1.70		(-0.2
% of total		0		3.56		1.47		0

---

[a] All data values reported as tpd adjusted to a normalized production rate, based on actual rock input and production rate.

[b] Weighted mean of materials composite (feed rock or products).

[c] Based on the steady-state composition of PW systems relative to water and fluoride balances.

[d] Accounted elsewhere in this positive water balance system; net PW makeup of 3446 tons [4681 t total (0% F) minus 1235 t overflow (0% F)], with an F uptake capacity at pond equilibrium (6500 ppm F) equal to 22.40 t F, corresponding to F removed from stacking water plus lime-treated overflow (22.68).

[e] Data on quantity and composition of recycle not available for inclusion.

[f] Based on percent of allowable maximum stack emission actually released.

TABLE X

F EQUILIBRATION PROCESSES IN AQUEOUS PHASE

$$HF + SiO_2 \rightleftarrows H_2SiF_6$$

$$F^- + Al(H_2O)_6{}^{3+} \rightleftarrows (AlF_x)^{3-x}$$

$$F^- + Mg^{2+} \rightleftarrows (MgF_x)^{2-x}$$

$$F + Al^{3+} + H_3PO_4 \rightleftarrows [AlF(H_3PO_4)]^{2+}$$

$$F + Al^{3+} + (H_2PO_4)^- \rightleftarrows [AlF(H_2PO_4]^+$$

$$F + Fe^{3+} + H_3PO_4 \rightleftarrows [FeF(H_3PO_4)]^{2+}$$

$$(SiF_6)^{2-} + Al(H_2O)_6{}^{3+} \rightleftarrows (AlF_6)^{3-} + SiO_2 \cdot nH_2O$$

TABLE XI

F EQUILIBRATION PROCESSES IN POND SOLIDS

Precipitation of F

$$F^- + Ca^{2+} \longrightarrow CaF_2$$

$$F^- + (AlF_6)^{3-} + (SiF_6)^{2-} + Ca^{2+} \longrightarrow Ca_4(SiF_6)(AlF_6)SO_4(F,OH) \cdot 10H_2O$$

$$F^- + (MgF_x)^{2-x} + Al^{3+} + Na^+ \longrightarrow (Na,Mg)_xAl_{2-x}F_6 \cdot 2H_2O$$

$$F^- + Mg^{2+} \longrightarrow MgF_2$$

Dissolution of F

$$NaKSiF_6 \xrightarrow{fast} (Na,K)^+,(SiF_6)^{2-}$$

$$Na_2SiF_6 \xrightarrow{slow} Na^+,(SiF_6)^{2-}$$

$$K_2SiF_6 \xrightarrow{v.slow} K^+,(SiF_6)^{2-}$$

$$(Na,K)_3AlF_6 \longrightarrow (Na,K)^+,(AlF_x)^{3-x}$$

$$Ca_3(AlF_6)_2 \cdot 4H_2O \longrightarrow CaF_{2(s)} + (AlF_x)^{3-x}$$

$$CaSiF_6 \cdot 2H_2O \longrightarrow CaF_{2(s)} + SiF_{4(g)}$$

TABLE XIII

RELATIONSHIP BETWEEN HF EMISSION AND SiO_2 CONTENT OF SOLUTION

SiO_2-Promoted Back Reaction

$$SiO_2 + 4HF \rightleftarrows SiF_4 + 2H_2O \qquad \text{IV}$$

$$SiF_4 + 2F^- \rightleftarrows (SiF_6)^{2-} \qquad \text{V}$$

Smirnova's Data (4% F soln. at 30°C)

Total Fg[a] (gm/m^3)	Mole ratio F/SiO_2 in solution	Mole ratio[b] F/SiO_2 in P.W.
0.0031	5	4.9
0.0067	6	6.5
0.0097	7	7.2

[a] Calculated from vapor pressure data.
[b] Examples from EPA (1974) composite data.

TABLE XII

POSSIBLE MOLECULAR SPECIES CONTRIBUTING TO TOTAL $F_{(g)}$ AND HIGH $HF:SiF_4$ MOLE RATIO

Molecular HF

$$HF \xrightleftharpoons{k\ =\ 10^{-3.2}} H^+ + F^- \quad \text{(2\% at pH 1.5)} \qquad \text{I}$$

Molecular H_2SiF_6

$$6HF + SiO_{2(aq)} \rightleftarrows [H_2SiF_6] + 2H_2O \qquad \text{II}$$

$$[H_2SiF_6] \rightleftarrows 2H^+ + 2(SiF_6)^{2-} \quad \text{(high K)} \qquad \text{III}$$

Molecular SiF_4

$$SiF_4 + 2H_2O \rightleftarrows 4HF + SiO_2 \quad \text{(vigorous)} \qquad \text{IV}$$

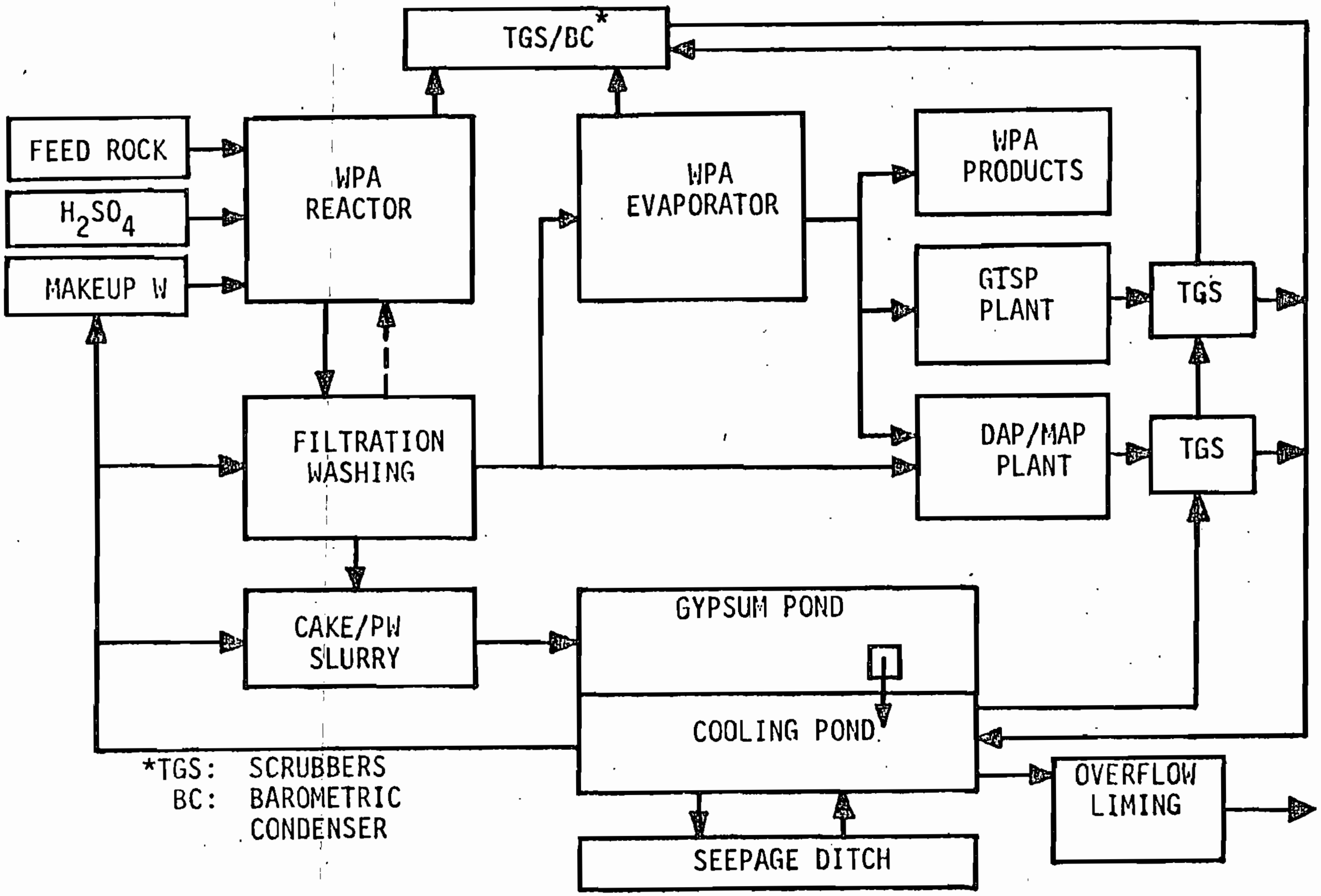
$$2F^- + SiF_4 \rightleftarrows (SiF_6)^{2-} \qquad \text{V}$$

$$3SiF_4 + 2H_2O \rightleftarrows 4H^+ + 2(SiF_6)^{2-} + SiO_2 \qquad \text{IV and V}$$

(for $F/SiO_2 \leq 6$: $[HF]_g >> [SiF_4];[H_2SiF_6] \sim 0$)

Figure 1

FLUORINE DISTRIBUTION: INTERRELATION OF GYPSUM POND SYSTEM TO THE TOTAL PROCESS



*TGS: SCRUBBERS
BC: BAROMETRIC CONDENSER

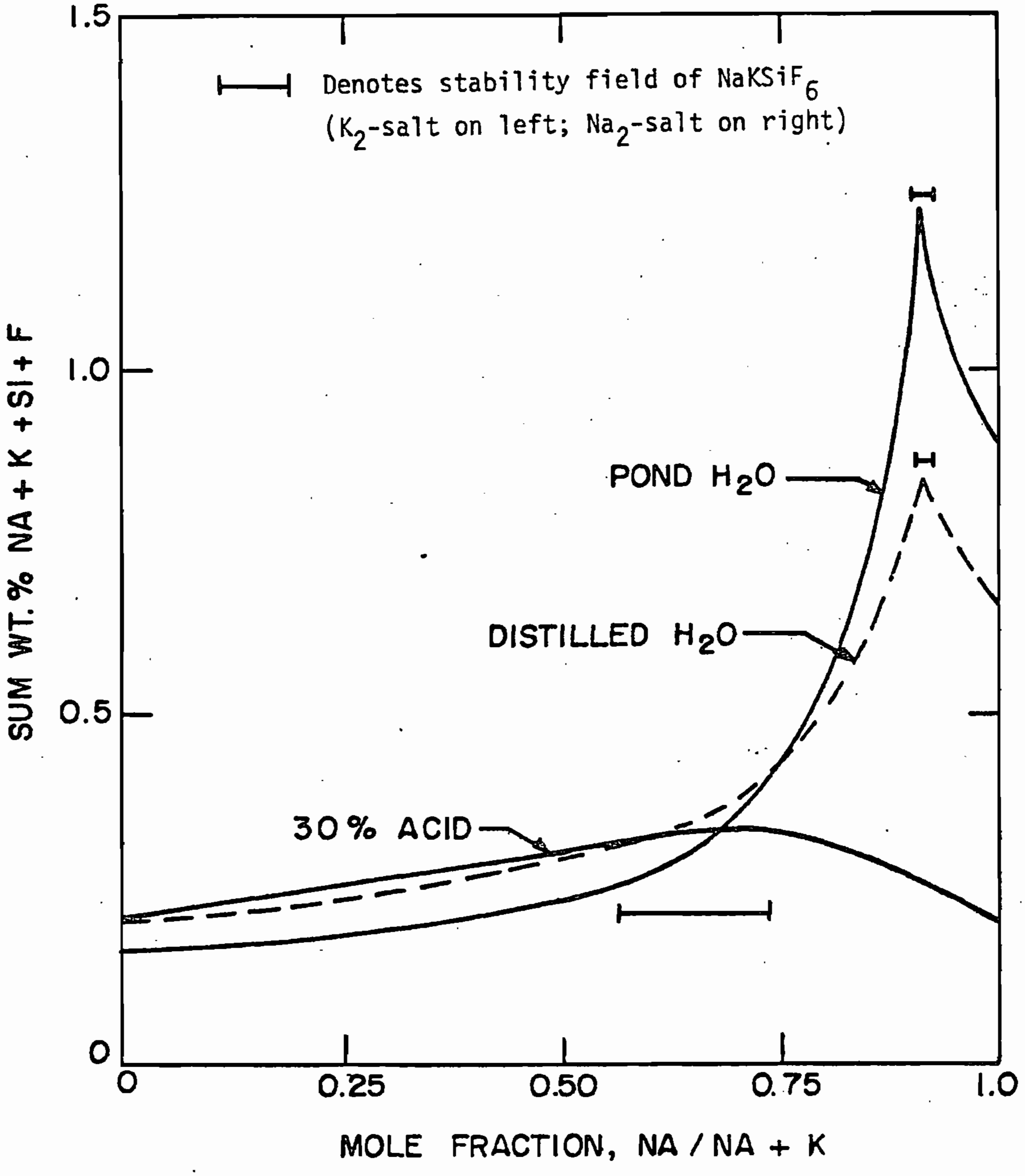

1.5
1.0
0.5
0
0
0.25
0.50
0.75
1.0
SUM WT. % NA + K + SI + F
MOLE FRACTION, NA / NA + K
Denotes stability field of NaKSiF6
(K2-salt on left; Na2-salt on right)
POND H2O
DISTILLED H2O
30% ACID

Figure 2

Figure 3

THE STORAGE POND SYSTEM: INTERRELATION OF FLUORINE DISTRIBUTION AND WATER MANAGEMENT

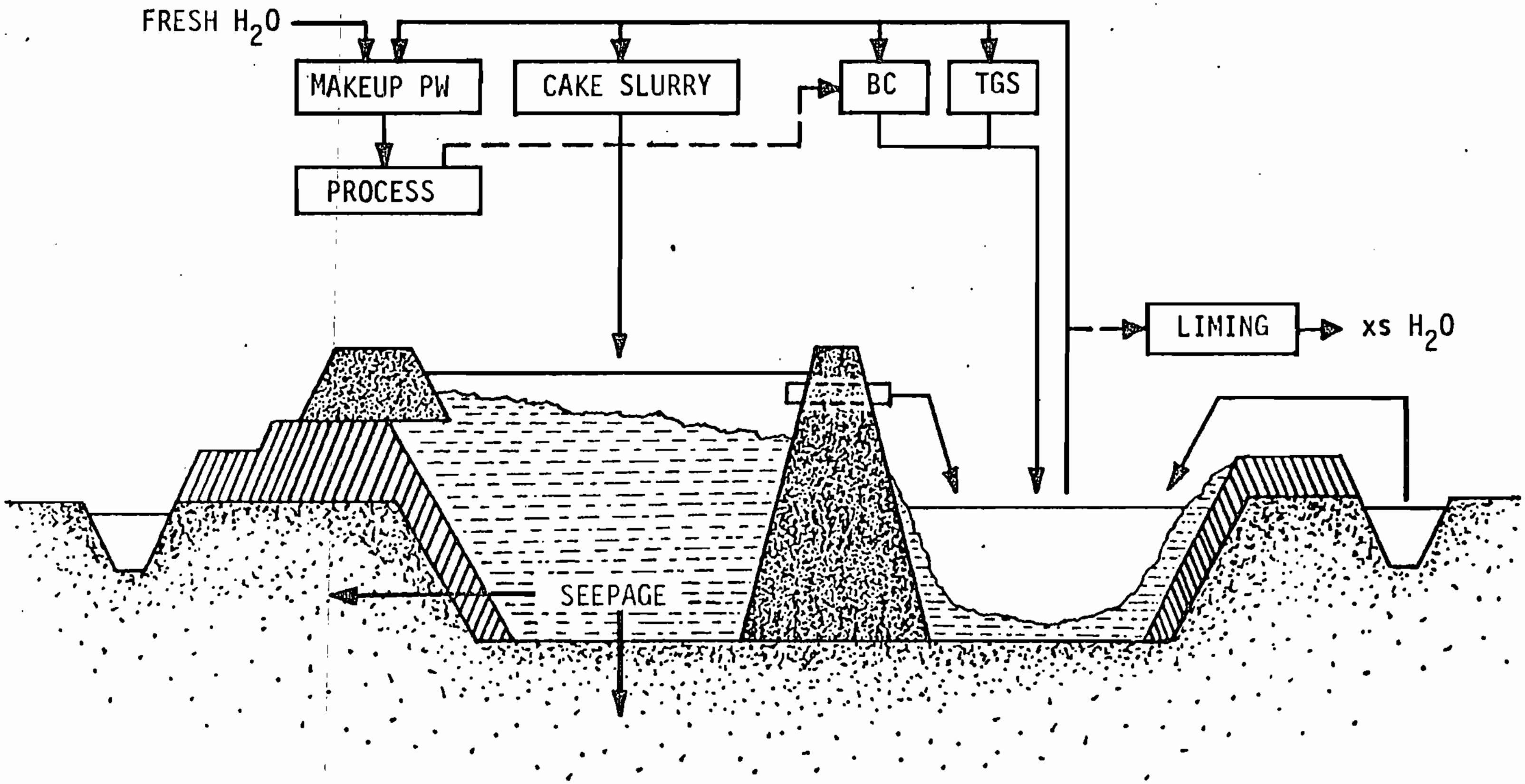
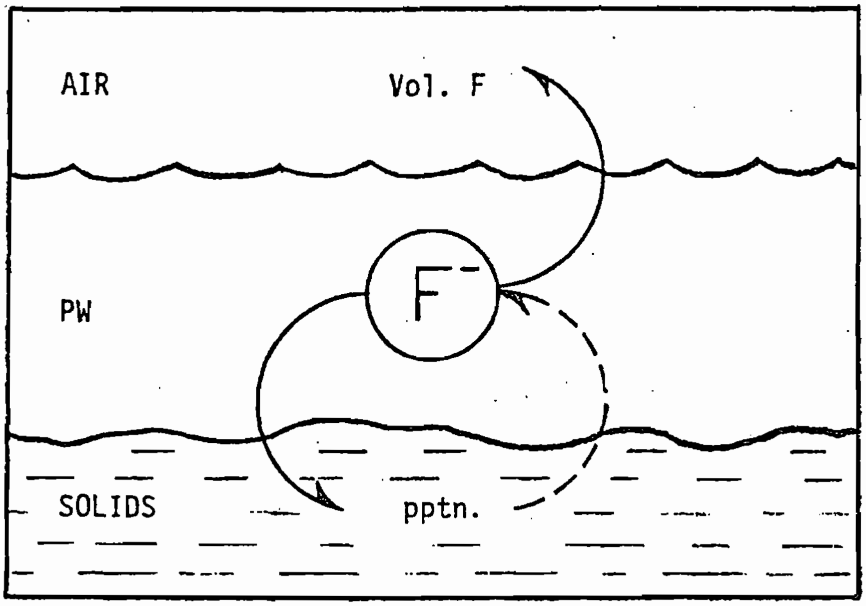


Figure 4

COMPETING FLUORIDE CHEMICAL EQUILIBRIA



Components

Vapor Phase: SiF_4, HF, H_2O

PW Phase: F^-, Al^{3+}, Mg^{2+}, Si^{4+}, $(Na,K)^+$, Fe^{3+}, Ca^{2+}, PO_4^{3-}, SO_4^{2-}

Solid Phase: Gypsum, F salts, inerts

Figure 5

HENRY'S LAW PLOT OF H_2SiF_6 VAPOR

PRESSURE DATA AT 85°-86°F

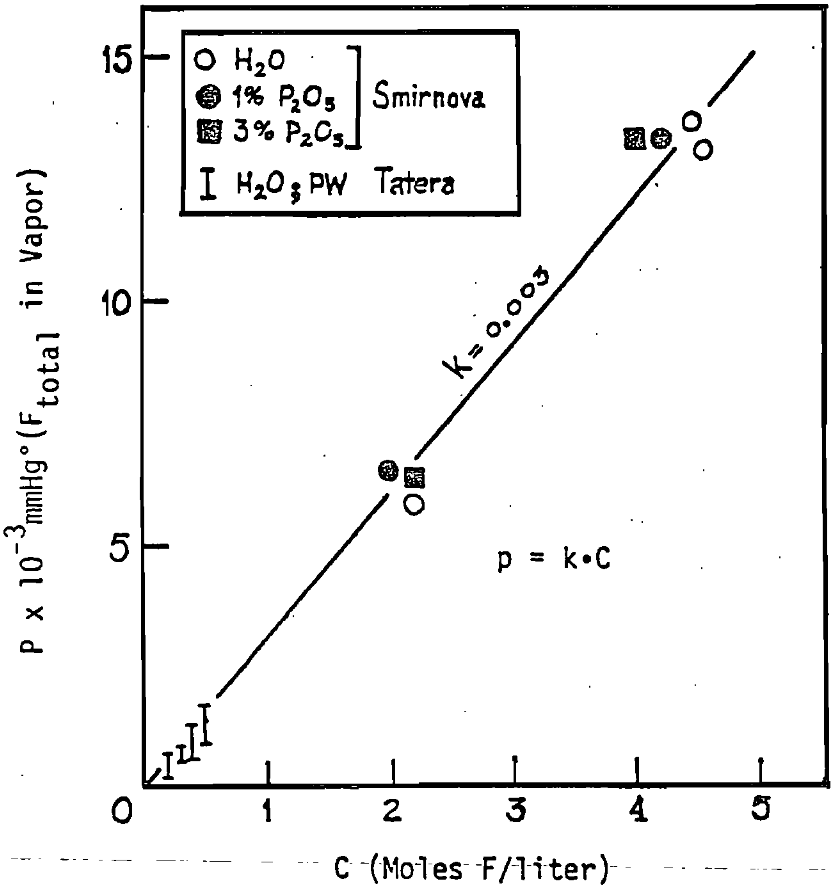


Figure 6

MOLE RATIO HF:SiF_4 IN VAPOR PHASE

VERSUS % F IN SOLUTION

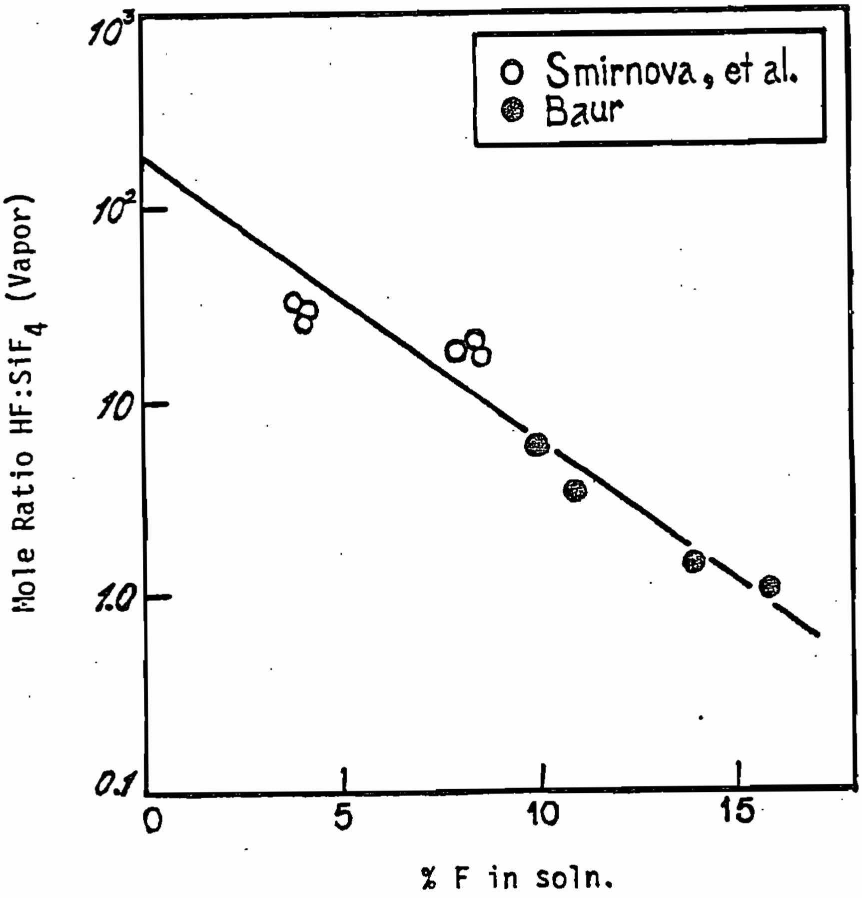
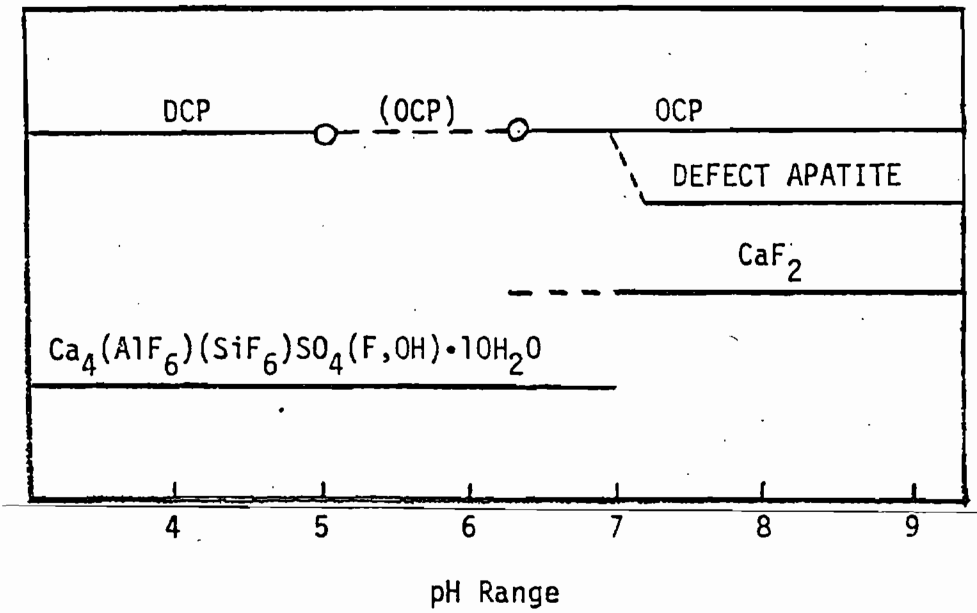


Figure 7

CHEMICAL MODELS OF F AND P_2O_5 REMOVAL BY LIME

Model phase systems	Predicted solids
HF-CaO-H_2O	CaF_2
CaO-P_2O_5-H_2O	DCP, OCP, apatite
HF-CaO-P_2O_5-H_2O	F-apatite + CaF_2

Observed solids



ATTACHMENT 2

GORDON F. PALM & ASSOCIATES, INC.

FLUORIDE EMISSIONS FROM GYPSUM PONDS
EVALUATION OF NEW WALES CHEMICALS, INC. AMBIENT AIR, PASTURE GRASS & CITRUS LEAF FLUORIDE DATA
FOR
1974, 1975, 1976 & 1977
FOR
FLORIDA PHOSPHATE INDUSTRY

PN-9700
6/20/78
REV. 1: 8/7/78
REV. 2: 4/2/79

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APPENDIX

CONCLUSIONS

1. IT WOULD BE DIFFICULT TO DESIGN A BETTER PROGRAM TO DETERMINE THE EFFECT OF GYPSUM WATER POND GASEOUS FLUORIDE EMISSIONS THAN THE MONITORING PROGRAM OF NEW WALES CHEMICALS, INC. FOR THEIR CHEMICAL PLANT SOUTH OF MULBERRY, FLORIDA.

2. THESE DATA REPRESENT A CLASSIC CASE SINCE FLUORIDES IN PASTURE GRASS, CITRUS LEAF, AND AMBIENT AIR WERE DETERMINED AROUND THE NEW CHEMICAL PLANT SITE FOR 14 MONTHS PRIOR TO START-UP AND FOR 33 MONTHS FOLLOWING START-UP — DURING A PERIOD WHEN GYPSUM POND WATER FLUORIDE CONTENT AND TEMPERATURE WERE INCREASING AND HEAT LOAD TO THE COOLING PONDS WAS INCREASING — CONDITIONS WHICH SHOULD TEND TO INCREASE GASEOUS FLUORIDE EMISSIONS FROM THE POND.

3. THE FLUORIDE DATA OBTAINED ARE CONCLUSIVE EVIDENCE THAT FLUORIDE EMISSIONS FROM THE GYPSUM WATER POND ARE TRIVIAL COMPARED TO THE TOTAL GASEOUS FLUORIDES IN THE AREA AROUND THE PLANT.

4. FURTHER STUDY OF GASEOUS FLUORIDE EMISSIONS FROM GYPSUM PONDS IS NOT ONLY UNWARRANTED AND COUNTER-PRODUCTIVE, BUT WOULD BE A WASTE OF VALUABLE VENTURE CAPITAL FUNDS.

RECOMMENDATIONS

A STUDY OF GASEOUS FLUORIDE EMISSIONS FROM GYPSUM PONDS SHOULD NOT BE MADE SINCE THE NEW WALES CHEMICALS, INC. FLUORIDE MONITORING DATA SHOW THAT THERE IS NO JUSTIFICATION FOR SUCH A STUDY.

I. INTRODUCTION

The Florida Department of Environmental Regulation (FDER) sent letters in late 1976 to a number of phosphate companies in central Florida requesting air permits for gypsum water ponds and estimates of fluoride emissions from these ponds. Although a number of studies (1)(2)(3) have been made in past years in an attempt to determine a fluoride emission factor (lb. F/day/acre) for these gypsum water ponds, these studies have been deficient in one regard or another, (4) and the scientific community is not satisfied that these predictions are indeed valid. Fluoride emission factors ranging from 0.1 to 10.0 lb. F/acre/day (4) have been proposed. Since the initial request by the FDER in late 1976, a number of meetings between FDER and the affected phosphate companies have been held and various air programs have been proposed by both sides and rejected or modified by both sides. Currently another proposed study is being actively considered. This program would verify air sampling and analytical techniques and develop a model to predict fluoride emission factors which would be checked for sensitivity and suitability prior to extensive air sampling in the field.

Recently, New Wales Chemicals, Inc., announced at one of the meetings that they have collected data on pasture grass fluorides, ambient air fluorides, and citrus leaf fluorides since 1974 which includes about 15 months prior to the start of their new chemical plant at New Wales, Florida which is located as shown in Fig. 1. These data have been filed monthly with the FDER office in Tampa, Florida.

The New Wales Chemicals, Inc. new chemical plant operation presents a <u>Classic Case</u> with regard to fluoride emissions from gypsum water ponds; i.e.:

1. Pasture grass, citrus, and ambient air fluoride levels were obtained for 15 months prior to the start-up of the new chemical plant and use of a gypsum water pond system.
2. The same type of data were obtained during the first 6-8 months of operation as the fluoride level in the gypsum water pond increased from zero to about 10,000 ppm F.
3. The same type of data were obtained during the next 2 years of operation as production rates increased, pond water temperature increased, and pond area increased.

IT WOULD BE DIFFICULT TO DESIGN A BETTER PROGRAM TO DETERMINE THE EFFECT OF FLUORIDE EMISSIONS FROM GYPSUM WATER PONDS. IF GYPSUM WATER PONDS ARE A SIGNIFICANT SOURCE OF ATMOSPHERIC FLUORIDE EMISSIONS, THIS SHOULD BE REFLECTED BY THE DATA COLLECTED BY NEW WALES CHEMICALS, INC.

IT WAS AGREED IN A MEETING IN LAKELAND, FLORIDA ON MAY 2, 1978, THAT THE FDER WOULD EVALUATE THE NEW WALES CHEMICALS, INC. DATA AND THAT THE PHOSPHATE INDUSTRY WOULD ALSO EVALUATE THESE DATA. THIS REPORT PRESENTS THE PHOSPHATE INDUSTRY'S EVALUATION OF THE NEW WALES DATA.

SAMPLING AND ANALYTICAL METHODS USED ARE IN THE APPENDIX OF THE REPORT.

II. SUMMARY

New Wales Chemicals, Inc. continues to monitor fluoride levels of citrus leaf at 7 sampling stations, ambient air at 3 sampling stations, and pasture grass at 10 sampling stations since 1974 as a condition of the operating permit for their new phosphate chemical plant at New Wales, Florida. These data have been evaluated to determine whether or not the gypsum water pond at New Wales is a significant contributor to fluorides in the area surrounding the new chemical plant.

Data were obtained for 14 months prior to plant start-up when the gypsum water pond was a mined-out cut containing uncontaminated water and for 33 months following start-up of the chemical plant. Since start-up in April 1974, the pond water fluorides have increased from essentially zero to a constant value of about 8,000-9,000 ppm F, pond water average temperatures have increased to about 96 °F (av. of inlet and outlet), production rate has increased from a baseline of 100% in 1975 to 319% in 1977.

It would be difficult to design a better program to determine the effect of gypsum water pond gaseous fluoride emissions and is considered to be a <u>Classic Case</u>. Of great significance is the fact that the New Wales chemical plant is probably the world's largest producer of acid P_2O_5. Data summaries are shown in Table 1 and represented graphically in Fig. 2.

In 1974 prior to start-up of the chemical plant, ambient air fluorides were 4.5 $\mu g/m^3$, citrus leaf fluorides were 56.8 ppm and pasture grass fluorides were 64.9 ppm. The plant site is about 4 miles from the nearest gypsum water pond and about 5 miles from the nearest phosphate rock dryers.

Chemical plant start-up was in April 1975 and during the balance of the year, fluoride level in the pond water increased from essentially zero to 5,900 ppm F for an 8-month average of 2,900 ppm F. The average of the inlet and exit water temperature was 90.6 °F. For 1975 (compared to 1974) ambient air fluorides dropped to 3.4 $\mu g/m^3$, citrus leaf fluorides dropped to 45.4 ppm and pasture grass fluorides went to 75.1 ppm.

By 1976, acid P_2O_5 production had increased to 267% (compared to 100% in 1975), pond water fluoride had increased to an average of 8,900 ppm F. Citrus leaf fluoride increased to 69.6 ppm and pasture grass fluoride dropped to 53.9 ppm. The ambient air fluoride sampling method was changed to the FDER method in May of 1976 and averaged 3.2 $\mu g/m^3$ for the final 7 months of 1976. Pasture grass fluorides were 53.9 ppm but only about 50% of the potential samples were obtained since grass was not available at the sample sites due to no growth.

However, in 1977, with gypsum pond fluoride levels and temperatures about the same as 1976, but with acid P_2O_5 production rate increased to 319%, citrus leaf fluorides dropped to 59.8 ppm (only 5.3% above 1974 levels with no operation) and ambient air level dropped slightly to 2.1 $\mu g/m^3$ from the 1976 level of 3.2 $\mu g/m^3$. Pasture grass fluorides went to 62.6 ppm (near the 1974 no operation level); however, only about 50% of the potential samples were obtained since grass was not available at the sample sites due to no growth.

It seems clear that gaseous fluoride emissions from the gypsum water pond are an insignificant factor in fluorides in the area around the chemical plant since fluoride levels in air, citrus, and grass were not influenced by increases of fluoride levels of the pond water or pond water temperature — all important variables in gaseous fluoride emissions from pond water. The variations in citrus leaf, ambient air, and pasture grass fluorides are probably caused by variations inherent in sampling methods, weather conditions, and possibly variations in gaseous fluoride emissions from stacks which are at a high elevation compared to the ground level gaseous fluoride emissions from the gypsum water pond.

In summary, this Classic Case comprising background fluoride data prior to start-up of a new large chemical plant, followed by fluoride monitoring for nearly three years of operations under conditions tending to increase gaseous fluoride emissions from a gypsum water pond, is conclusive evidence that fluoride emissions from gypsum water ponds are trivial compared to the total gaseous fluorides in the area around the plant. Further study of gaseous fluoride emissions from gypsum ponds is not only unwarranted and counter-productive, but would be a waste of valuable venture capital funds.

TABLE 1
SUMMARY
FLUORIDE MONITORING DATA
NEW WALES CHEMICALS, INC.
NEW WALES, FLORIDA

	YEAR				
AVERAGE VALUES	1974(1)	1975(2)	1976(2)	1977(2)	1978(2)
POND WATER, PPM F, AV.	0	2900	8900	8300	
POND WATER TEMP., °F(3)	-	90.6	96.3	96.5	
RELATIVE ACID P2O5 PROD. RATE, %	0	100 [illegible]	267 [illegible]	319 [illegible]	
AV. AMBIENT AIR FLUORIDE, μG/M^3(4)	4.5	3.4	3.2(6)	2.1	1.7(7)
AV. CITRUS LEAF FLUORIDE, PPM	56.8	45.4	69.6	59.8	
COMPARISON WITH 1974(5)	100%	79.9%	122.5%	105.3%	
AV. PASTURE GRASS FLUORIDE, PPM	64.9	75.1	53.9(8)	62.6(8)	
COMPARISON WITH 1974	100%	116%	83%	96%	

NOTES:
1. MONITORING, SAMPLING, AND ANALYSES PERFORMED BY ENVIRONMENTAL SCIENCE & ENGINEERING, INC.
2. MONITORING, SAMPLING, AND ANALYSES PERFORMED BY NEW WALES CHEMICALS, INC.
3. AVERAGE OF INLET AND OUTLET TEMPERATURES.
4. WATER SOLUBLE FLUORIDES.
5. PRIOR TO OPERATION OF CHEMICAL PLANT.
6. CHANGED TO FDER SAMPLING METHOD IN MAY 1976.
7. 3 MONTHS AVERAGE.
8. ONLY ABOUT 50% OF POTENTIAL SAMPLES TAKEN FOR THE YEAR DUE TO NO GRASS GROWTH.

III. DISCUSSION

A. Foreword

Data available from New Wales Chemicals, Inc. together with additional information requested for this industry study are as follows:

1. Pond water fluoride levels and pond inlet and outlet temperatures from April 1975 (Start-up) through December 1977. Since gaseous fluoride emissions from pond water are a function of fluoride vapor pressure, which is a function of fluoride concentration & temperature, these data should indicate the relative potentials for gaseous fluoride emissions.
2. Relative acid P2O5 production rates of the chemical plant with production for the first 9 months of 1975 used as a base rate of 100%. Since the production rate determines the temperature of the pond water entering the pond and the amount of water evaporated in the gypsum pond (in order to cool and recycle the water), the gaseous fluoride emissions should be influenced by these factors.
3. Pasture grass fluoride data from February 1974 through December 1977 for 10 stations surrounding the New Wales chemical plant.
4. Citrus leaf fluoride data from February 1974 through December 1977 for 7 stations surrounding the New Wales chemical plant.
5. Ambient air fluoride data from January 1974 through March 1978 for 3 stations surrounding the New Wales chemical plant.

B. Pond Water Fluoride Levels and Temperatures and Pond Water Area

New Wales data for pond water fluoride levels and temperatures are summarized in Table 2. Prior to start-up, the gypsum pond contained mine water and during the year before operation had essentially a zero fluoride level and could not emit any gaseous fluorides.

After start-up in April 1975, the pond water fluoride level climbed to 5,900 ppm F by December and averaged 2,900 ppm F for the first 8 months of operation. Average pond water temperature for 1975 was 90.6°F with an average inlet of 94.7°F and average outlet of 86.6°F. 1975 acid P2O5 production rate was taken as a base of 100%.

In 1976, as acid P2O5 production rate rose to 267%, the fluoride level in the pond continued to increase, reached its highest level by March, and then varied downward due to rainfall and other factors. Average for the year was 8,900 ppm F. The pond water inlet temperature averaged 103.8° F and outlet averaged 88.7° F for an average of 96.3° F, or an increase of 5.7° F over 1975.

For 1977, the production rate increased to 319% but pond fluoride level remained essentially constant at 8,300 ppm F av. and the average temperature was about the same — 96.5° F (av. inlet and outlet).

Pond water fluoride vapor pressures are directly proportional to fluoride concentration (in the F ranges encountered) and increase exponentially with the absolute temperature. Therefore, it would be expected that fluoride emissions in 1976 and 1977 should be higher than those of 1975 when lower fluoride concentrations and a slightly lower temperature prevailed.

If gaseous fluorides emissions from the gypsum water pond are a significant factor in fluoride emissions in the area, then the ambient air, pasture grass fluorides, and citrus leaf fluorides should show a marked increase for the years 1976 and 1977 over 1975 and be even higher than those of 1974 before the plant was in operation.

C. Relative Acid P2O5 Production Rates

Using 1975 as a base year of 100%, relative acid P2O5 production rates increased to 267% in 1976 and 319% in 1977 as shown in Table 3. As production rates increase, the amount of process heat sent to the gypsum pond increases and the pond water temperature entering the pond increases. Exit pond temperatures also increase unless the size of the pond is increased. The amount of gaseous fluorides evolved by the various processes also increases with production rate and are removed in scrubbers using the recycling gypsum pond water. In general, increased production rates would tend to increase gaseous fluoride emissions from gypsum water ponds and this should be reflected in ambient air fluoride levels, pasture grass fluoride levels, and citrus leaf fluoride levels provided that gypsum pond fluoride emissions are a significant source of gaseous fluorides in the area around the chemical plant.

D. Pasture Grass Fluoride Data

Pasture grass fluoride data for 10 sampling stations located as shown on Figure 3 are contained in Tables 4, 5, 6, and 7 for the years 1974, 1975, 1976, and 1977. One station was located adjacent to the chemical plant site and other stations at distances varying from about 1.6 miles to about 5 miles in all directions.

Data are about 90% complete for each station for each month in 1974 and 1975 but are only about 50% complete for 1976 and 1977 since grass was not growing at the sample sites at various times and grass samples could not be obtained. A summary of pasture grass fluoride data is shown in Table 8.

In 1974, prior to operation of the chemical plant, all 10 stations were sampled for each month except January 1977, and the average pasture grass fluoride was 64.9 ppm F.

For 1975, with plant start-up in April using fresh water in the gypsum pond, a fluoride level of 5,900 ppm F was obtained by December 1975. Average pond water temperature ((inlet & outlet) ÷ 2) was 90.6° F and fluorides averaged 2,900 ppm F for the 8 months. Production of acid P_2O_5 during this 9 months of 1974 has been used as a base production of 100%. All 10 stations were sampled for each month except December 1975 and the average pasture grass fluoride was 75.1 ppm F or 16% higher than 1974.

During 1976, acid P_2O_5 production increased to 267% compared to 1975, the pond water fluoride increased to 8,900 ppm F (av.), and the average pond water temperature increased to 96.3° F. Pasture grass fluoride samples were not obtained in January, February, and November, and only sporadically in March, April, October, and November. The average fluoride for those sampled, 47% of potential samples, was 53.9 ppm F (17% less than 1974).

Due to the large number of samples missing for 1976, it is hard to compare the pasture grass fluoride data with previous years; however, since these represent the fluoride values of the grass that was available for forage, they should be representative of available forage. Citrus leaf fluoride data which is about 90% complete for 1976 may be a better indicator of the effects of gaseous fluorides in the area.

By 1977, acid P_2O_5 production had increased to 319% compared to 1975, the pond water fluoride level was 8,300 ppm F or about the same as 1976. Average pond water temperature was 96.5° F — about the same as 1976. Pasture grass fluoride samples were not obtained in January, October, November, December, and were sporadic in April and May and only 53% of potential samples were obtained. Average of all samples was 62.6 ppm F, 96% of 1974. Again, it is difficult to compare pasture grass fluorides with previous years; however, these values are representative of the available forage. Citrus leaf fluoride data which is about 99% complete for 1977 may be a better indicator.

In summary, pasture grass fluoride averages for all stations did not materially change from the 1974 levels with no plant operating during 1975, 1976, and 1977, although acid P_2O_5 production rates, pond water fluoride levels and temperature all increased substantially. This strongly indicates that the gypsum water pond is not a significant source of gaseous fluorides in the area.

E. CITRUS LEAF FLUORIDE DATA

CITRUS LEAF FLUORIDE DATA FOR 7 SAMPLING STATIONS LOCATED AS SHOWN ON FIGURE 4 ARE CONTAINED IN TABLES 4, 5, 6, AND 7 FOR THE YEARS 1974, 1975, 1976, AND 1977. STATIONS WERE LOCATED ABOUT 1.5 TO 4 MILES FROM THE CHEMICAL PLANT.

SUMMARIES OF CITRUS LEAF FLUORIDE DATA ARE SHOWN IN TABLES 9 & 10 AND FIGURE 5. DATA ARE OVER 90% COMPLETE FOR EACH OF THE FOUR YEARS AND SHOULD GIVE A GOOD INDICATION OF THE SIGNIFICANCE OF GASEOUS FLUORIDE EMISSIONS FROM THE GYPSUM WATER POND.

IN 1974, PRIOR TO OPERATION OF THE CHEMICAL PLANT, ALL 7 STATIONS WERE SAMPLED FOR EACH MONTH EXCEPT JANUARY 1974 AND ONE STATION MISSED IN FEBRUARY AND APRIL. THE AVERAGE CITRUS LEAF FLUORIDE WAS 56.8 PPM F.

FOR 1975, WITH PLANT START-UP IN APRIL USING FRESH WATER IN THE GYPSUM POND, A FLUORIDE LEVEL OF 5,900 PPM F WAS OBTAINED BY DECEMBER 1975 AND AVERAGED 2,900 PPM F FOR THE 8 MONTHS. AVERAGE POND WATER TEMPERATURE WAS 90.6° F.

PRODUCTION OF ACID P2O5 DURING THIS 9 MONTHS OF 1974 HAS BEEN USED AS A BASE PRODUCTION OF 100%. ALL 7 STATIONS WERE SAMPLED EACH MONTH EXCEPT FOR FEBRUARY 1975 AND THE AVERAGE CITRUS LEAF FLUORIDE WAS 45.4 PPM F OR 20% LOWER THAN IN 1974 WITHOUT PLANT OPERATION.

DURING 1976, ACID P2O5 PRODUCTION INCREASED TO 267% COMPARED TO 1975, THE POND WATER FLUORIDE INCREASED TO 8,900 PPM F (AV.), THE AVERAGE POND WATER TEMPERATURE INCREASED TO 96.3° F. CITRUS LEAF FLUORIDES WERE SAMPLED AT ALL 7 STATIONS EACH MONTH EXCEPT FOR DECEMBER 1976 AND ONE STATION MISSED IN AUGUST, SEPTEMBER, AND OCTOBER. AVERAGE CITRUS LEAF FLUORIDES WERE 69.6 PPM F OR 23% HIGHER THAN 1974 WITHOUT PLANT OPERATION.

BY 1977, ACID P2O5 PRODUCTION HAD INCREASED TO 319% COMPARED TO 1975, AND, THE POND WATER FLUORIDE LEVEL WAS 8,300 PPM F OR ABOUT THE SAME AS 1976. AVERAGE POND WATER TEMPERATURE WAS 96.5° F — ABOUT THE SAME AS 1976. CITRUS LEAF FLUORIDES, HOWEVER, DROPPED FROM 1976 TO AN AVERAGE VALUE OF 59.8 PPM FOR 1977 — ONLY 5% MORE THAN FOR 1974 WITH NO PLANT OPERATION.

IN SUMMARY, CITRUS LEAF FLUORIDE AVERAGES FOR ALL STATIONS DID NOT MATERIALLY CHANGE FROM THE 1974 LEVELS WITH NO PLANT OPERATION DURING 1975, 1976, AND 1977, ALTHOUGH ACID P2O5 PRODUCTION RATES, POND WATER FLUORIDE LEVELS, AND WATER TEMPERATURE ALL INCREASED SUBSTANTIALLY. THIS VARIATION FROM YEAR TO YEAR IN THE CITRUS LEAF FLUORIDE LEVELS, BASED ON CONSIDERATION OF THESE FACTORS, WOULD SEEM TO BE CAUSED BY VARIANCES IN SAMPLING AND POSSIBLY WEATHER CONDITIONS AND NOT DUE TO FLUORIDE EMISSIONS FROM THE GYPSUM WATER POND.

IN 1977, AT THE HIGHEST ACID P_2O_5 PRODUCTION RATE, AND WITH A HIGH FLUORIDE LEVEL IN THE POND WATER AND THE HIGHEST AVERAGE POND WATER TEMPERATURE, THE CITRUS LEAF FLUORIDE LEVEL WAS ONLY 105% OF 1974, THE YEAR BEFORE PLANT OPERATION. SINCE THIS IS PROBABLY THE LARGEST ACID P_2O_5 COMPLEX IN THE WORLD IN TERMS OF PRODUCTION, IF THE GYPSUM POND WATER IS A SIGNIFICANT CONTRIBUTOR TO FLUORIDE EMISSIONS, IT IS NOT EVIDENT FROM THE CITRUS LEAF FLUORIDE DATA. ONE CAN ONLY CONCLUDE THAT GASEOUS FLUORIDE EMISSIONS FROM THE GYPSUM WATER POND ARE AN INSIGNIFICANT FACTOR IN FLUORIDE UPTAKE BY CITRUS.

F. AMBIENT AIR FLUORIDE DATA

AMBIENT AIR FLUORIDE DATA FOR 3 SAMPLING STATIONS LOCATED AS SHOWN ON FIGURE 6 ARE CONTAINED IN TABLES 11, 12, 13, 14, & 15 FOR THE YEARS 1974, 1975, 1976, 1977, 1978, AND ARE SUMMARIZED IN TABLE 16. STATION 1 IS ABOUT 2 MILES WSW OF THE CHEMICAL PLANT SITE, STATION 2 ABOUT 1 MILE DUE NORTH, AND STATION 3 ABOUT 3 MILES ALMOST DUE EAST. SUMMARIES OF AMBIENT AIR FLUORIDE DATA ARE GIVEN IN TABLE 16 AS SHOWN ON FIGURE 7.

AMBIENT AIR SAMPLES FOR 1974, 1975, AND THE FIRST 5 MONTHS OF 1976 WERE COLLECTED USING A TWO-IMPINGER METHOD. AFTER MAY 1976, THE METHOD WAS CHANGED TO THE FDER ONE-IMPINGER METHOD.

PRIOR TO PLANT START-UP IN 1974, AMBIENT AIR FLUORIDE AVERAGES WERE $4.5\ \mu g/m^3$ AND DURING THE FIRST YEAR OF OPERATIONS IN 1975 (STARTING OPERATIONS IN APRIL), THE AVERAGE VALUES WERE $3.4\ \mu g/m^3$ OR 24% LOWER THAN NO PLANT OPERATION AT ALL.

IN 1976, AMBIENT AIR FLUORIDES RANGED FROM 5.6 TO $18.5\ \mu g/m^3$ FOR THE FIRST 5 MONTHS AND AVERAGED $12.6\ \mu g/m^3$. STARTING IN MAY 1976, THE SAMPLING METHOD WAS CHANGED TO THE FDER METHOD AND THE AVERAGE FOR THE LAST 7 MONTHS WAS $3.2\ \mu g/m^3$. DURING THIS PERIOD THE ACID P_2O_5 PRODUCTION RATE WAS 267%, THE POND WATER FLUORIDES 8,900 PPM, AND THE WATER TEMPERATURE 96.3° F.

IN 1977, ACID P_2O_5 PRODUCTION RATE INCREASED TO 319%, POND WATER FLUORIDES AND TEMPERATURE REMAINED ABOUT CONSTANT AT 8,300 PPM F AND 96.5° F RESPECTIVELY. AMBIENT AIR FLUORIDES DECREASED TO $2.1\ \mu g/m^3$ OR 66% OF 1976. THIS LOWER LEVEL HAS CONTINUED FOR THE FIRST 3 MONTHS IN 1978 WHICH AVERAGED $1.7\ \mu g/m^3$.

IN SUMMARY, AMBIENT AIR FLUORIDES DECREASED 25% FROM THE 1974 LEVELS DURING THE FIRST YEAR OF PRODUCTION IN 1975. IN 1977, AMBIENT AIR FLUORIDES WERE 34% LESS THAN THE LAST 7 MONTHS OF 1976 (FDER METHOD). THESE DATA ARE CLEAR EVIDENCE THAT FLUORIDE EMISSIONS FROM THE GYPSUM POND WATER ARE A MINISCULE PORTION OF THE AMBIENT AIR FLUORIDE LEVELS AROUND THE CHEMICAL PLANT AND GYPSUM WATER POND. THIS WAS STRONGLY INDICATED BY PASTURE GRASS FLUORIDE LEVELS AND IS CLEARLY SHOWN BY CITRUS LEAF FLUORIDE LEVELS. THE PHYSICAL CHEMISTRY OF THE GYPSUM POND WATER SYSTEM REQUIRES THAT GASEOUS FLUORIDE EMISSIONS FROM THE POND MUST INCREASE AS POND WATER FLUORIDE LEVEL AND TEMPERATURE INCREASE. APPARENTLY THIS INCREASE WAS TRIVIAL AS REFLECTED BY THE AMBIENT AIR FLUORIDE DATA.

REFERENCES

1. Cross, F. L. and Ross, R. W., J. Air Pollution Control Assoc., 19, No. 1.

2. Tatera, B. S., Parameters Which Influence Fluoride Emissions from Gypsum Ponds, Ph.D. Dissertation, University of Florida (1970).

3. King, W. R. and Farrell, J. K., Fluoride Emissions from Phosphoric Acid Gypsum Ponds, EPA sp EPA 650-2-74-095, Oct. 1974.

4. Environmental Science and Engineering, Inc., Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry, EPA Contract No. 68-02-1330 Task No. 3, June 1978, Administrative Issue.

FIG. 1

LOCATION OF NEW WALES CHEMICALS, INC.

MULBERRY, FLORIDA

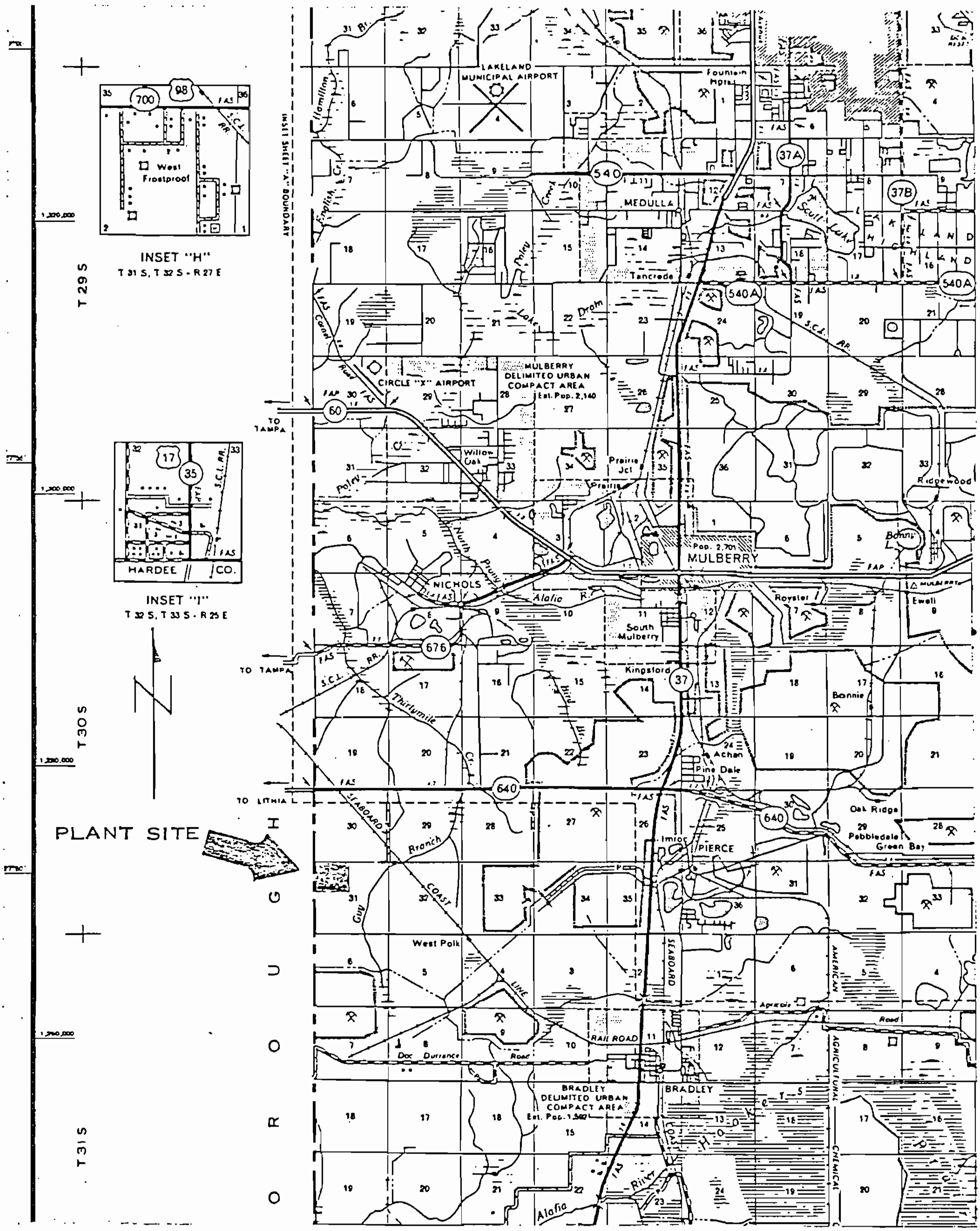


FIG. 2

SUMMARY
FLUORIDE MONITORING DATA
NEW WALES CHEMICALS, INC.
MULBERRY, FLORIDA

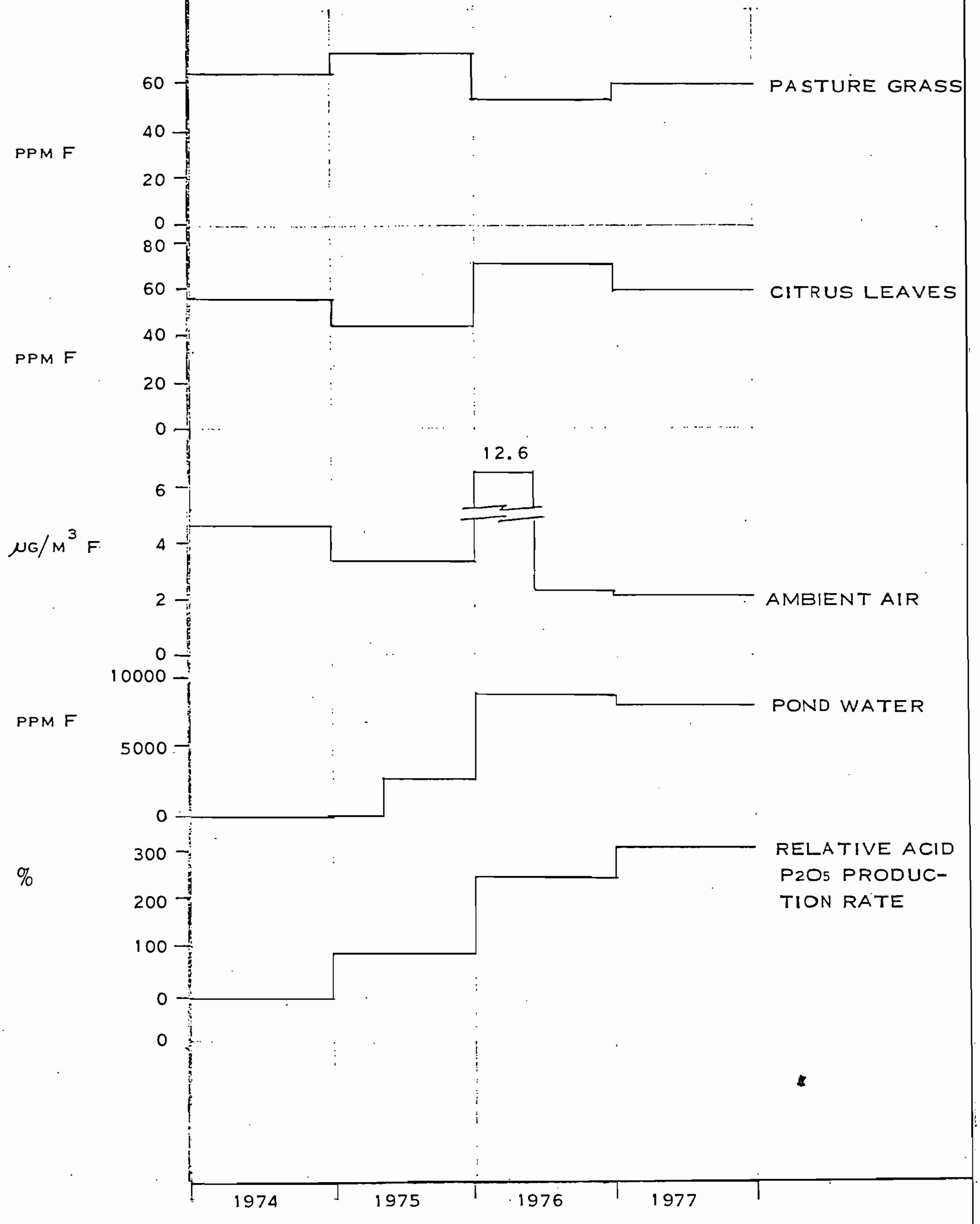
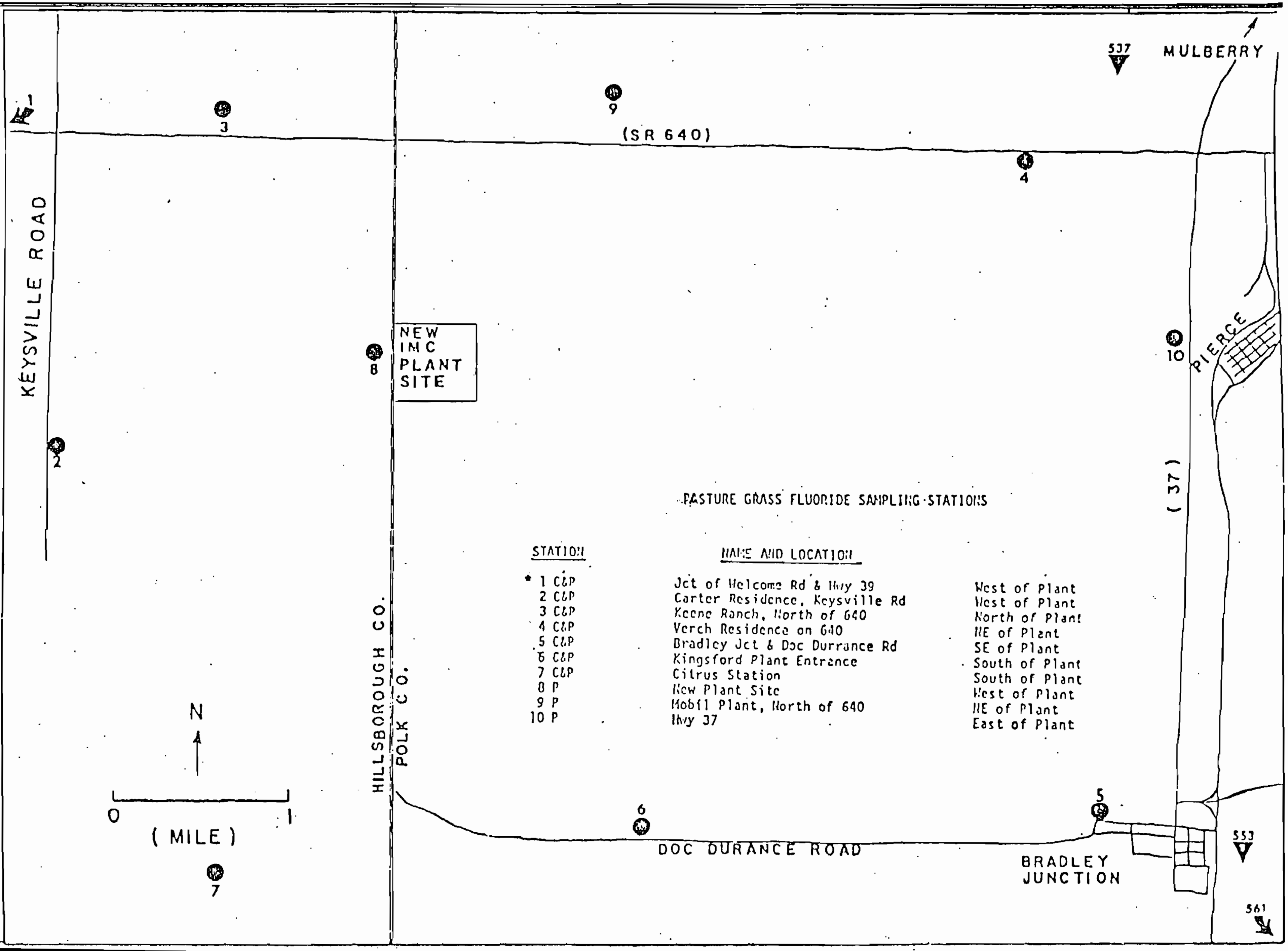


FIG. 3

PASTURE GRASS FLUORIDE SAMPLING LOCATIONS



PASTURE GRASS FLUORIDE SAMPLING STATIONS

STATION	NAME AND LOCATION	
* 1 C&P	Jct of Welcome Rd & Hwy 39	West of Plant
2 C&P	Carter Residence, Keysville Rd	West of Plant
3 C&P	Keene Ranch, North of 640	North of Plant
4 C&P	Verch Residence on 640	NE of Plant
5 C&P	Bradley Jct & Doc Durrance Rd	SE of Plant
6 C&P	Kingsford Plant Entrance	South of Plant
7 C&P	Citrus Station	South of Plant
8 P	New Plant Site	West of Plant
9 P	Mobil Plant, North of 640	NE of Plant
10 P	Hwy 37	East of Plant

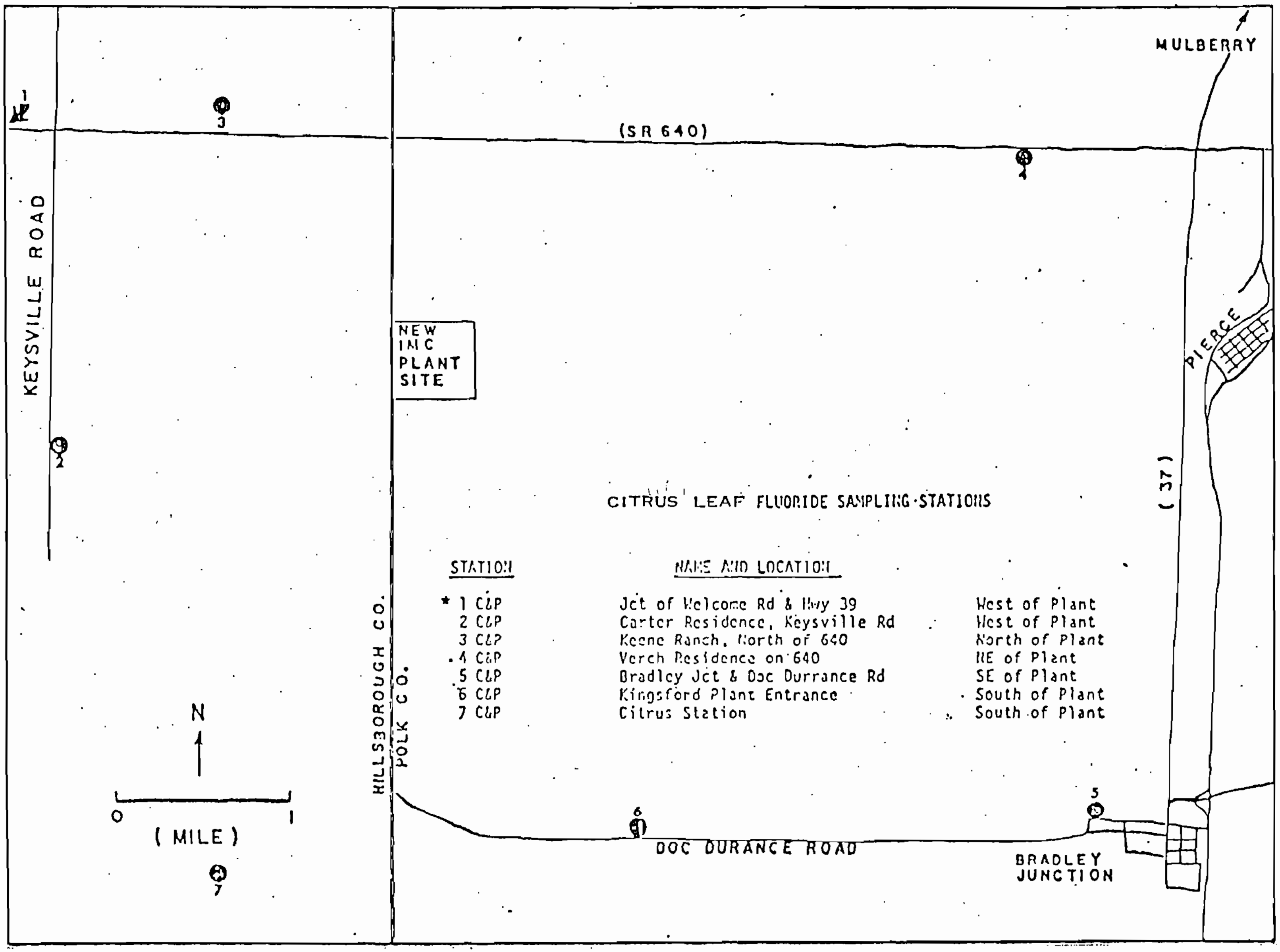
GORDON F. PALM & ASSOCIATES, INC.

FIG. 4

CITRUS LEAF FLUORIDE SAMPLING STATIONS

STATIONS 13 AND 27 WERE SITES FOR A 12-MONTH FLUORIDE SURVEY OF FLORIDA ORANGE GROVES, 1961-1962 (REF. 5)

✳ STATION LOCATED OFF THE MAP



CITRUS LEAF FLUORIDE SAMPLING STATIONS

STATION	NAME AND LOCATION	
* 1 C&P	Jct of Welcome Rd & Hwy 39	West of Plant
2 C&P	Carter Residence, Keysville Rd	West of Plant
3 C&P	Keene Ranch, North of 640	North of Plant
4 C&P	Verch Residence on 640	NE of Plant
5 C&P	Bradley Jct & Doc Durrance Rd	SE of Plant
6 C&P	Kingsford Plant Entrance	South of Plant
7 C&P	Citrus Station	South of Plant

FIG. 5

AVERAGE MONTHLY CITRUS LEAF FLUORIDES

NEW WALES CHEMICALS, INC.

MULBERRY, FLORIDA

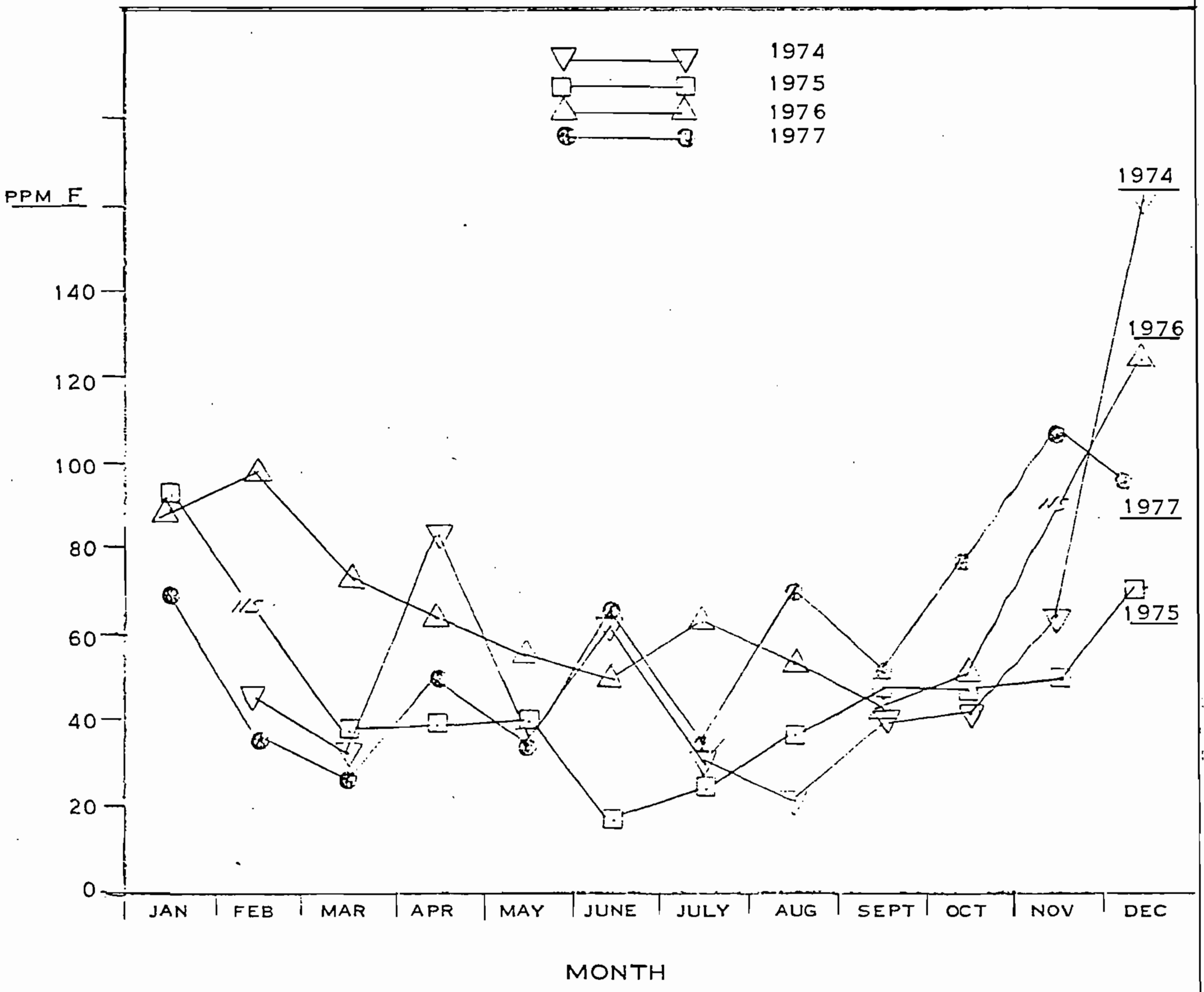
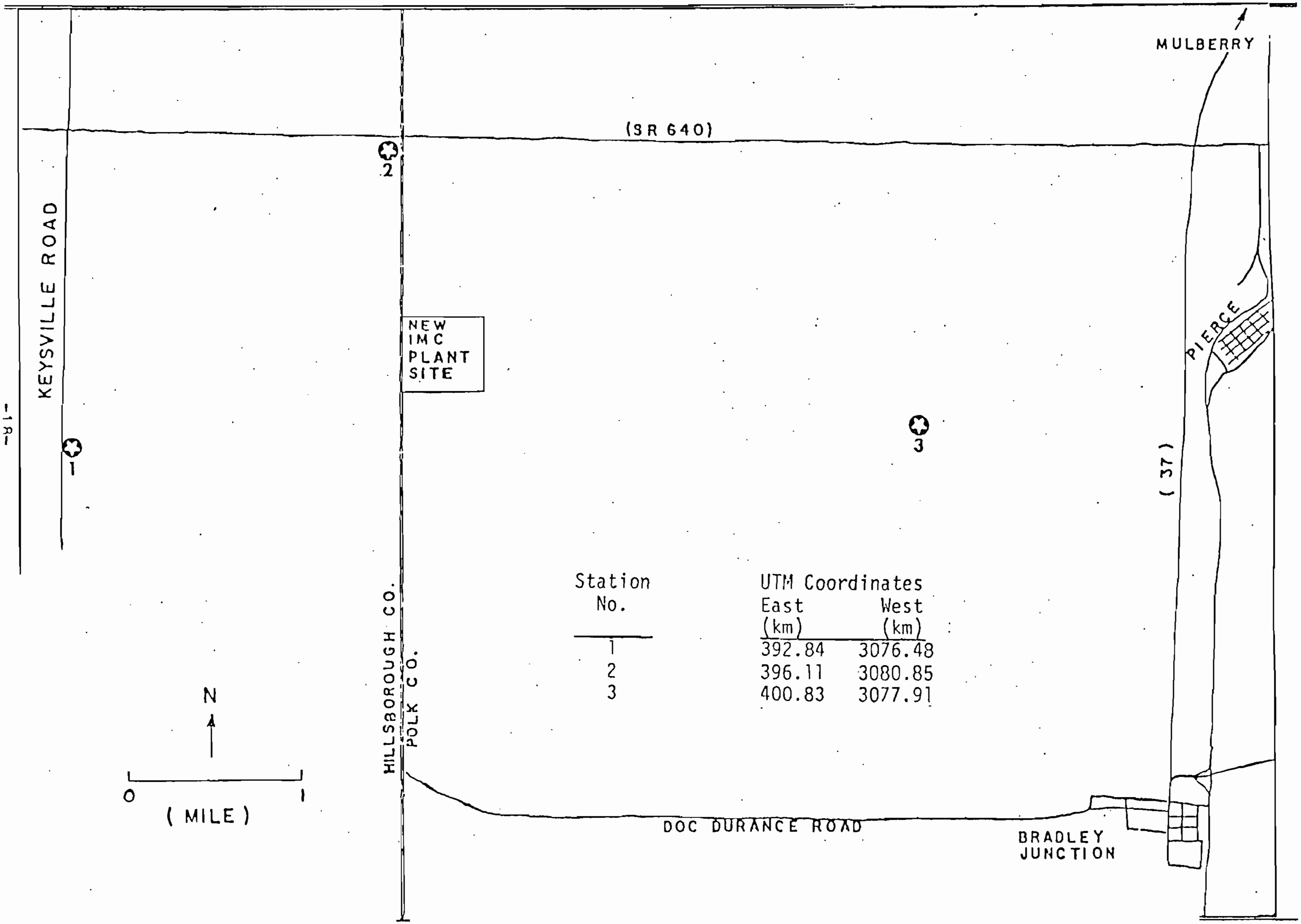


FIG. 6

AMBIENT AIR FLUORIDE SAMPLING STATIONS



Station No.	UTM Coordinates East (km)	West (km)
1	392.84	3076.48
2	396.11	3080.85
3	400.83	3077.91

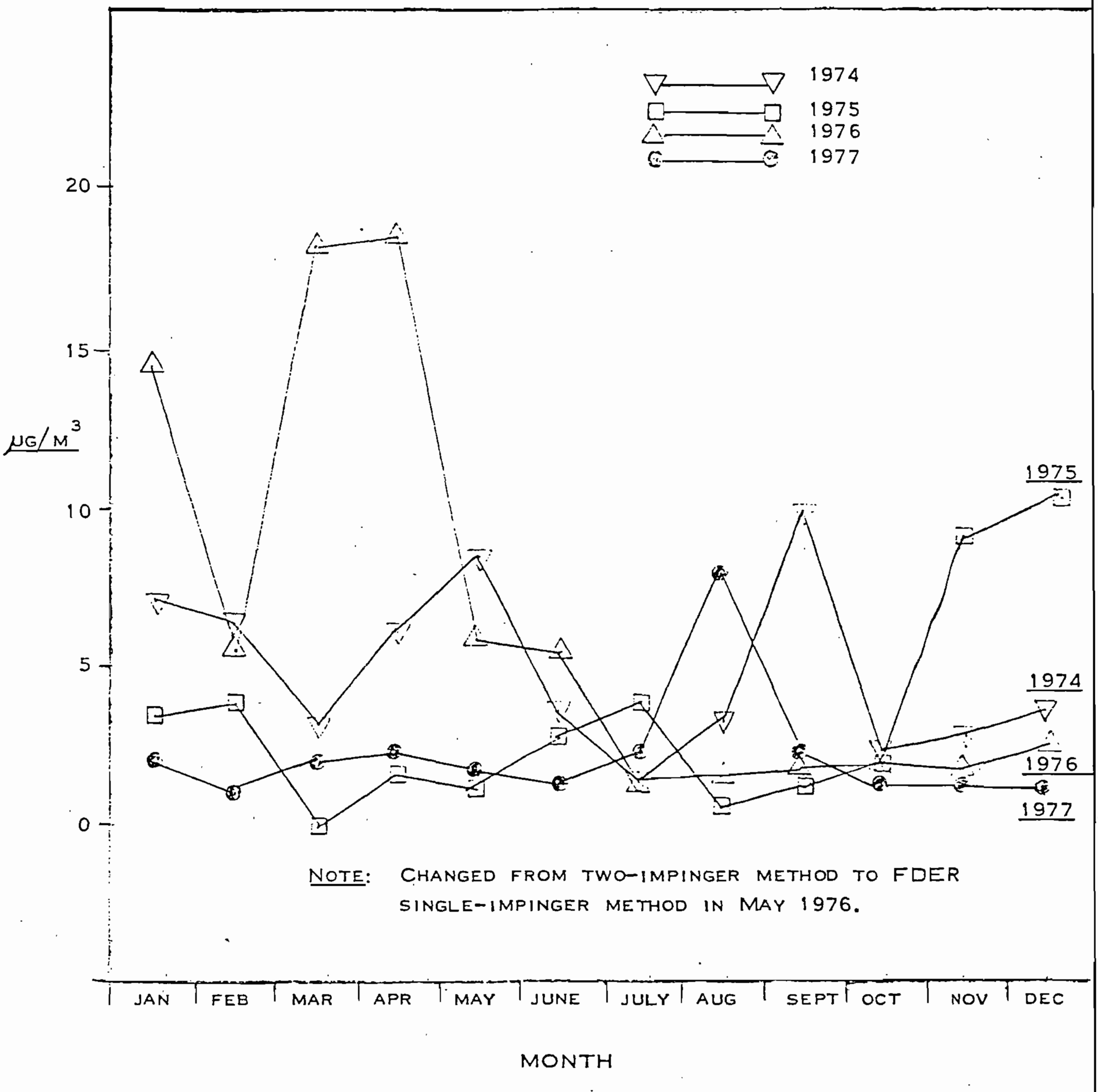
GORDON F. PALM & ASSOCIATES, INC.

FIG. 7

AVERAGE MONTHLY AMBIENT AIR FLUORIDES

NEW WALES CHEMICALS, INC.

MULBERRY, FLORIDA



NOTE: CHANGED FROM TWO-IMPINGER METHOD TO FDER SINGLE-IMPINGER METHOD IN MAY 1976.

TABLE 2

POND WATER - NEW WALES CHEMICALS, FLORIDA
AVERAGE MONTHLY ANALYSIS OF F AND P_2O_5
AND AVERAGE MONTHLY TEMPERATURE

	Analysis		Pond Temperature, °F	
Month & Year	% F	% P_2O_5	Inlet	Outlet
1975				
April	-	0.009	91.0	77.6
May	0.047	0.048	80.8	78.0
June	0.061	0.10	91.5	82.8
July	0.06	0.17	101.5	90.0
August	0.34	0.21	98.3	92.0
September	0.32	0.30	98.4	90.0
October	0.41	0.28	100.0	90.0
November	0.48	0.28	99.0	89.0
December	0.59	0.34	87.8	80.6
Average	0.29		94.7	86.6
1976				
January	0.62	0.4	83.3	72.0
February	0.95	0.49	97.0	76.5
March	1.15	0.6	105.6	90.8
April	1.15	0.64	108.0	92.8
May	1.12	0.56	107.8	88.5
June	0.92	0.58	109.5	99.5
July	0.96	0.54	104.8	99.0
August	0.89	0.53	115.5	99.8
September	0.68	0.45	113.6	95.2
October	0.64	0.45	110.0	94.0
November	0.8	0.51	99.5	81.0
December	0.77	0.53	91.3	75.3
Average	0.89		103.8	88.7
1977				
January	0.84	0.6	90.0	71.8
February	0.83	0.63	96.0	76.3
March	0.85	0.68	100.5	80.5
April	0.91	0.70	101.3	86.3
May	0.96	0.70	107.8	87.5
June	0.95	0.69	112.7	94.3
July	0.83	0.58	115.2	94.6
August	0.77	0.60	115.3	92.8
September	0.71	0.60	117.0	92.5
October	0.72	0.61	107.3	87.7
November	0.79	0.67	108.5	89.0
December	0.79	0.71	105.0	86.0
Average	0.83		106.4	86.6

TABLE 3
RELATIVE PRODUCTION RATES OF P_2O_5 IN PHOSPHORIC ACID PLANT AT NEW WALES CHEMICALS COMPLEX

Description	Year			
	1974	1975	1976	1977
Relative Production Rate	0%	100%(1)	267%	319%

Note: 1. One train in the phosphoric acid plant started up in April 1975. In May, the second train was started. In 1975, P_2O_5 production was taken at 100% for a base.

ATTACHMENT 3

COOLING POND HEAT RELEASE
NEW WALES CHEM. CO. – POLK COUNTY, FLA.

For a flow thru pond the relationship between pond temperature, heat load and pond surface area can be expressed by the following expression (5):

$$\frac{T-E}{T_o-E} = \exp\left[-\frac{KA}{62.4\,Q}\right]$$

Where T = Temperature of water at any point in the pond, °F.

T_o = Pond water discharge temperature, °F

E = Equilibrium temperature, °F

A = Pond area, ft^2

Q = Pond water flow rate, ft^3/day

K = Exchange coefficient, Btu/ft^2/day/°F = 425

For New Wales:

T = 112° F at inlet of pond, and
T_o = 92° F at pond exit under most severe conditions
E = 91° F (assumed to represent worst conditions)
Q_{exist} = 110,000 gpm = 21.1×10^6 ft^3/day
$Q_{proposed}$ = 132,500 gpm = 25.4×10^6 ft^3/day

K = **450** BTU/ft^2/day/°F

Calculate: A exist = A_e
A proposed = A_p

Existing

$$\frac{112-91}{92-91} = \frac{1}{e^{\left[\frac{450\,A_a}{62.4\times 21.1\times 10^6}\right]}}$$

$$0.34\,A_a\times 10^{-6} = \ln 21$$

$$A_a = 8.95\times 10^6\ \text{ft}^2$$
$$= 206\ \text{Acres}$$

Proposed

$$\frac{112-91}{92-91} = \frac{1}{e^{\left[\frac{450\,A_P}{62.4\times 25.4\times 10^6}\right]}}$$

$$A_P = 10.71\times 10^6\ \text{ft}^2$$
$$= 246\ \text{Acres}$$

Pond Water Temp Range (°F)	ΔT (To − T) (°F)	$\frac{T - E}{To - E}$	F^- Conc. in Vapor at Equilib (4) (ppm)	Existing Heat Load			Proposed Heat Load		
				Area at Temp Range (acres)	Cumulative Area (acres)	Emission Factor*	Area at Temp Range (acres)	Cumulative Area (acres)	Emission Factor*
112 - 111	1	0.95	7.9	3.3	3.3	26.1	3.9	3.9	30.8
111 - 110	2	0.90	7.6	3.4	6.7	25.8	4.2	8.1	31.9
110 - 109	3	0.86	7.3	3.7	10.4	27.0	4.4	12.5	32.1
109 - 108	4	0.81	7.0	3.8	14.2	26.6	4.6	17.1	32.2
108 - 107	5	0.76	6.7	4.1	18.3	27.5	4.9	22.0	32.8
107 - 106	6	0.71	6.4	4.3	22.6	27.5	5.2	27.2	33.3
106 - 105	7	0.67	6.1	4.6	27.2	28.1	5.6	32.8	34.2
105 - 104	8	0.62	5.8	5.0	32.2	29.0	6.0	38.8	34.8
104 - 103	9	0.57	5.6	5.4	37.6	30.2	6.4	45.2	35.8
103 - 102	10	0.52	5.4	5.8	43.4	31.3	7.1	52.3	38.3
102 - 101	11	0.48	5.2	6.4	49.8	33.3	7.7	60.0	40.0
101 - 100	12	0.43	5.0	7.1	56.9	35.5	8.5	68.5	42.5
100 - 99	13	0.38	4.8	7.9	64.8	37.9	9.5	78.0	45.6
99 - 98	14	0.33	4.6	9.0	73.8	41.4	10.8	88.8	49.7
98 - 97	15	0.29	4.4	10.3	84.1	45.3	12.5	101.3	55.0
97 - 96	16	0.24	4.2	12.3	96.4	51.7	14.7	116.0	61.7
96 - 95	17	0.19	4.0	15.0	111.4	60.0	18.1	134.1	72.4
95 - 94	18	0.14	3.9	19.3	130.7	75.3	23.2	157.3	90.5
94 - 93	19	0.10	3.8	27.2	157.9	103.4	32.8	190.1	124.6
93 - 92	20	0.05	3.7	46.6	204.5	172.4	56.1	246.2	207.6
92	20		3.6	95.5	300**	343.8	53.8	300**	193.7
				300**		1279.1	300**		1319.7

* Fluoride emissions from ponds are proportional to (1) Pond area, (2) Fluoride vapor pressure, and (3) wind speed (Reference [2]). For comparing existing and proposed pond fluoride emissions it is assumed that wind speed is constant. Therefore, the Emission Factor is equal to the product of the area and the fluoride concentration in the vapor over the pond water at equilibrium.

$$\text{Increase in Emissions} \propto \frac{1319.7 - 1279.1}{1279.1} \times 100 = 3.2\%$$

** Pond area at New Wales is 300 acres

ATTACHMENT 4

United States
Environmental Protection
Agency

Region 4
345 Courtland Street, NE
Atlanta, GA 30308

EPA 904/9-78-012-A
JULY 1978

DRAFT

EPA

Environmental Impact Statement

Occidental Chemical Company
Swift Creek Chemical Complex
Hamilton County, Florida

Resource Document
Volume I

A1.3 EXISTING SUWANNEE RIVER CHEMICAL COMPLEX (SRCC) FACILITIES PLUS PHASE I EXPANSION AT SUWANNEE RIVER CHEMICAL COMPLEX

A1.3.1 INTRODUCTION

Operation of the existing Suwannee River Chemical Complex (SRCC) began in the fall of 1966 with the production of sulfuric acid (SA), granular triplesuperphosphate (GTSP), diammonium phosphate (DAP), superphosphoric acid (SPA), and merchant phosphoric acid (MPA), and by-product gypsum (GYP), based on a wet process phosphoric acid production capability of 220,000 STPY P_2O_5. A defluorinated phosphate rock animal feed ingredient unit (Polyphos) was added in 1970. In 1975, an expansion was completed to increase wet phosphoric acid production capacity to the present level of 550,000 short tons per year.

Engineering for Phase I of the Russian SPA project (as an "expansion" of SRCC) started in April 1977, construction in August 1977. Start-up is planned for October 1978.

SRCC is located in Hamilton County in North Florida, on a level plot of about 120 acres, north of White Springs, Florida; and east of State Road 137, which intersects U.S. Highway 41 between White Springs and Jasper, Florida, as shown on Figure 1.4-1. UMT coordinates are E328320, N3368820.

A1.3.2. CHEMICAL PLANT DESCRIPTION

A1.3.2.1 Products

Final products are SA, GTSP, DAP, SPA, MPA and Polyphos. Some by-product gypsum is shipped from the Chemical Complex for use as a soil conditioner. The gypsum has a Ra-226 content of 14 pCi/g compared to a phosphate rock content of rate of 18 pCi/g (Table 3.5-1-Summary Document). Ground phosphate rock was used extensively in the past as a slow release fertilizer.

A1.3.2.2 Capacity

Capacity of the SRCC is 550,000 short tons per year of P_2O_5 as wet process phosphoric acid used in the production of the final products. Sufficient sulfuric acid will be produced on-site to satisfy requirements. Phosphate rock will be supplied from the existing (and adjacent) Suwannee River Mine (SRM).

A1.3.2.3 Raw Materials

Sulfur, ammonia, and caustic soda will be supplied by rail car, by truck, and phosphate rock by conveyor belt.

A1.3.2.4 Process Units

Intermediates and final products will be processed or produced on-site using the existing facilities which consist of a phosphate rock grinding plant, three wet process phosphoric acid plants, four contact sulfuric acid plants, a GTSP plant, two DAP plants, and a Polyphos plant. New facilities to be added in Phase I consist of a phosphoric acid clarification plant and two SPA evaporators. Two existing SPA plants will be idled and a solvent extraction (S-X) pilot plant may be operated a few weeks per year.

2.2.2.3.2 Fluoride in the Environment -- Since fluoride emissions from ponds cannot be estimated with a reasonable degree of accuracy, and since emissions from ponds cannot be reasonably simulated with air quality models, the impact of existing fluoride emissions was determined by:

1. Measuring gaseous fluoride concentrations in the ambient air;
2. Measuring the fluoride concentrations in grass;
3. Observing the effects of fluorides on cattle; and
4. Observing the effects of fluorides on vegetation.

Airborne Fluorides

Gaseous fluorides in the ambient air have been measured at five monitoring sites (Figure 2.2-7), since November 27, 1977. The program is continuing.

Samples are collected at each monitoring site once every sixth day. The sample is collected by drawing ambient air through two Greenburg-Smith impingers in series. Each impinger contains 200 milliliters of 0.1 N sodium hydroxide solution. The sampling rate is approximately 0.5 cubic feet per minute. The samples are analyzed with a specific ion electrode.

The monitoring data through April, 1978 are summarized in Table 2.2-7. It will be noted that there is very little spatial variation in ambient fluoride levels. The average concentrations range from 0.7 to

1.0 micrograms per cubic meter. The average concentration for all sites is 0.8 micrograms per cubic meter. 24-hour concentrations range from 5.1 micrograms per cubic meter to 0.1 micrograms per cubic meter.

As a point of comparison the Florida Department of Environmental Regulation, in 1976, proposed the following ambient air quality standards for fluorides (FDER, 1976):

1. Annual - 0.71 micrograms per cubic meter;
2. For any 30-day period - 1.43 micrograms per cubic meter;
3. For any 24-hour period - 4.44 micrograms per cubic meter.

Fluoride in Grass

One potential economic impact of fluoride in the environment is the effect to livestock caused by ingestion of forage materials containing fluorides. In significant concentrations, the fluorides create a condition known as fluorosis. This manifests itself in mottling and/or softening of the teeth of livestock, and in alterations of bone structure.

The threshhold concentration in forage material at which these effects become noticeable in beef and dairy heifers is 40 ppm of a soluble fluoride and 60 ppm of an insoluble fluoride. (National Academy of Sciences, 1974). For other species, higher dietary fluoride levels can be tolerated.

To determine the level of fluorides in potential forage materials near the Occidental site, ten sampling locations were selected. Eight of these represented potential pasture land, one site was on the dike of a cooling water pond and one site was located an intermediate distance from the cooling water pond. These sampling sites are shown in Figure 2.2-7. In addition to these sites a background site was selected in Gainesville, Florida.

Grass samples were collected at each of these sites monthly, beginning in December 1977. Approximately 200 to 300 grams of grass was collected at each site. In the laboratory each sample was placed in an ultrasonic cleaner with cold water for fifteen minutes. The purpose of this step was to remove particulate fluoride from the leaf of the grass prior to analysis. Both the washed grass sample and the wash water were analyzed for fluoride.

The fluoride levels in the grass samples collected during the period December 1977-June 1978 are presented in Table 2.2-7. Is should be recognized that this period represents the time of year when grass fluoride levels are the highest. This is the result of little or no growth during the winter months and low rainfall during the spring months.

Monthly fluoride concentrations ranged from 5 to 88 ppm total fluoride in grass away from the existing chemical plant. The fraction of fluorides contained in the grass (soluble) averaged 78 percent. The fraction contained on the surface of the leaf (insoluble) averaged 22 percent.

The grass from the monitoring site located on the dike of the cooling water pond exhibited an average fluoride concentration of 232 ppm with approximately 71 percent of the fluoride being contained in the leaf of the grass. Grass a moderate distance (800 meters) from a cooling water pond had an average fluoride concentration of 71 ppm with approximately 67 percent of the fluoride being contained in the grass leaf. Fluoride concentrations in grass samples collected in Gainesville, Florida during this period averaged 19 ppm.

Observed Effects of Fluorides on Livestock

Cattle from three sites were examined in April 1978 by a veterinarian experienced in the effects of fluorosis (Crum, 1978). The study was made to determine if cattle born and raised near the Occidental site are affected by fluorides in the forage provided them.

The area is utilized primarily for pulpwood production. There are, however, a number of small farms and pasturelands located within a 5-mile radius of the plant. The three sites investigated are shown on Figure 2.2-7.

All cattle examined were raised in the area where they were examined. They had free access to pasture grasses year-round and in some cases received locally grown hay and corn as a winter feed supplement.

The cattle were examined to determine if individual animals had consumed excessive fluorides during their early dentition periods (first five years of age) as evidenced by changes in the structure and wear of teeth. Twenty-one animals, ranging in age from 10 months to 13 years, were examined. Eight animals were examined at the south and east sites and five were examined at the southwest site.

The examination showed the greatest effect to be that defined:

> Slight Effect - slight mottling of enamel, best observed as horizontal striations with transmitted light; may have slight staining but no increase in normal rate of wear (National Academy of Sciences, 1974).

This effect was exhibited in a total of nine teeth from six of the 21 animals examined. The number of teeth showing effects in these six animals ranged from one to three.

The examination further revealed the cattle to be free from skeletal fluorosis. It was concluded that none of the effects were sufficient to cause a loss of productivity.

Effects of Fluorides on Vegetation

Surveys conducted in the area since 1974 have revealed no significant fluoride effects on vegetation anywhere in the area. The latest survey was conducted in March 1978. The only effects noted at that time were moderate tip necrosis on a few pine trees located on the dike forming one of the cooling water ponds. Maple, sweet gum, willow and other shrubby material on the dikes showed no fluoride effects. Pine trees, a few hundred meters from the ponds, were normal (Brandt, 1978).

Observations in the vicinity of the Swift Creek site revealed no fluoride effects.

Table 2.2-7 Summary of Ambient Air and Grass Fluoride Concentration Data for November 1977 - June 1978, Occidental Chemical Company, Hamilton County, Florida

Site(1)		Fluoride Concentration									
		Ambient Air (µg/m³)				Grass (mg/kg)					
							Average				
Air	Grass	Number 24-hr Samples	Max.	Min.	Avg.	Number Monthly Samples	Soluble(2)	Insoluble(3)	Total	Max. Total	Min. Total
A	10	24	5.1	0.1	1.0	7	34.3	8.7	43.0	81.9	8.3
B	9	24	4.3	0.1	0.8	7	33.4	6.2	39.6	69.3	7.6
C	8	24	3.1	0.2	0.8	7	35.9	10.5	46.4	88.1	10.9
D	5	21	3.1	0.1	0.7	7	28.4	8.7	37.1	52.9	13.4
E	4	22	2.5	0.3	0.9	5	17.6	9.3	26.9	50.1	6.1
	1					7	20.6	4.4	25.0	55.8	5.2
	2					7	32.3	7.5	39.8	81.4	11.6
	3					7	32.1	5.8	37.9	72.2	9.7
	6					7	229.0	94.0	323.0	474.0	205.0
	7					7	47.3	23.3	70.6	137.4	30.6
Background						5	16.3	2.3	18.6	36.1	6.7

(1) See Figure 2.2-7

(2) Soluble Fluoride is defined as that remaining in leaf after washing for 15 min. in ultrasonic cold water bath.

(3) Insoluble Fluoride is defined as that washed from leaf surface.

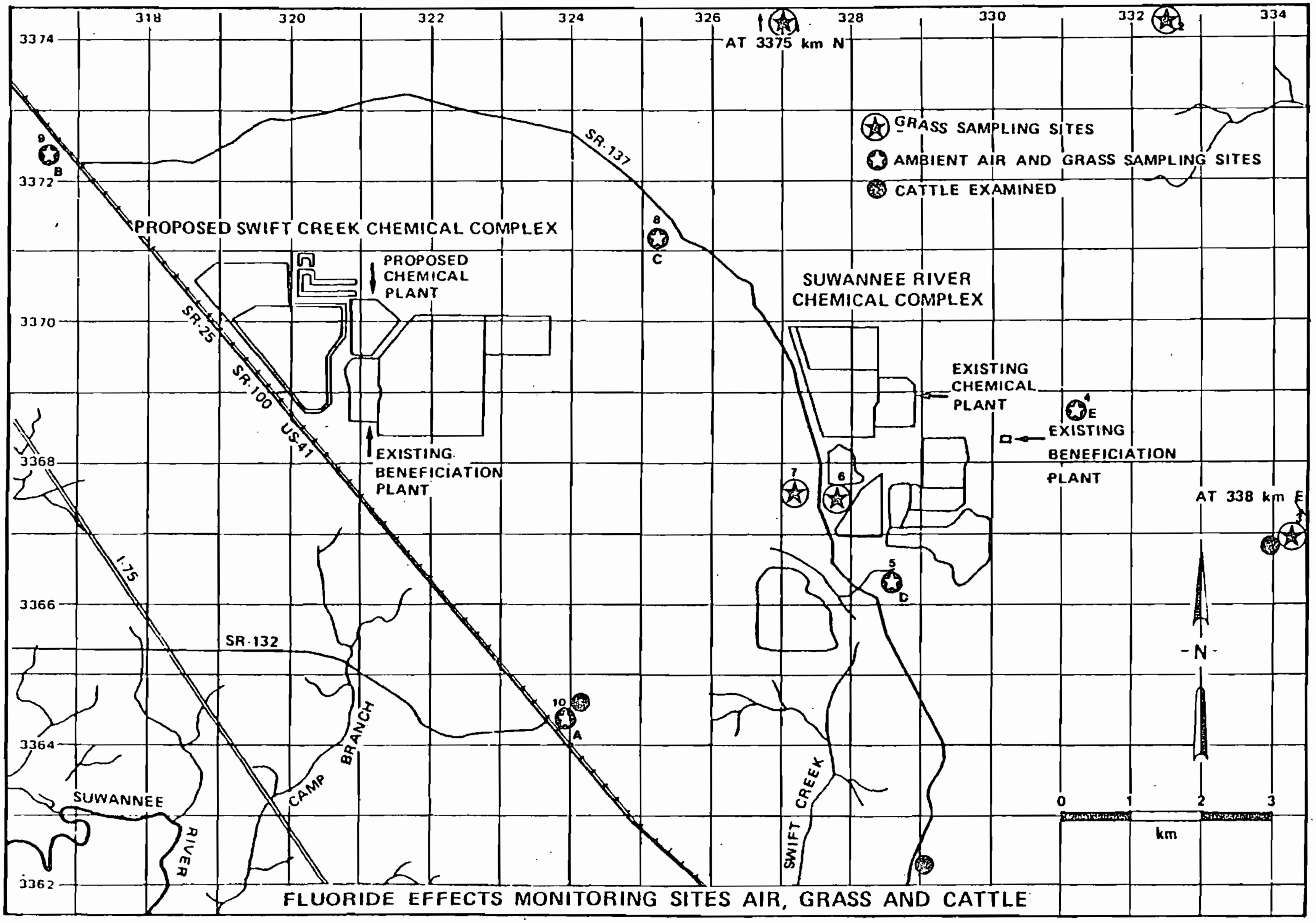

FLUORIDE EFFECTS MONITORING SITES AIR, GRASS AND CATTLE

FIGURE 2.2-7

APPENDIX A

(Section 2.2)

FIELD SURVEYS FOR FLUORIDE EFFECTS ON CATTLE AND VEGETATION

WHITE SPRINGS, FLORIDA
Dr. Brandt
SURVEY

[illegible]
[illegible]
12-12-77

November 15 and 16, 1977

I surveyed the area around the White Springs, Florida, plant of Occidental Chemical Company for possible effects of air pollutants on the surrounding vegetation as a result of plant operations. I also examined the area around the Swift Creek Mine area to identify any potential impact from the proposed super phosphoric acid operations at that site. Mr. John Wester, of Occidental Chemical Company, accompanied me.

None of the vegetation exhibited any symptoms suggestive of chronic sulfur dioxide injury. At the time of my visit normal senescense had obscurred any chronic symptoms on much of the deciduous vegetation. However, the remaining desiduous material and the pine appeared normal for the season and site.

An area along SR 137 showed evidence of a moderately severe burn from sulfur dioxide, possibly in combination with sulfuric acid mist. The affected area starts at the road, a mile due east of the chemical plant complex and extends irregularly west of the road for roughly 0.4 miles and for approximately 1.2 miles in a north-south direction along the road. The major injury occurred in an irregularly shaped plantation of slash pine about eight years old. The date of the episode is unknown. The symptoms were apparently fully developed when first noted in the middle of the summer. At the time of my visit, secondary infections and other normal changes have confounded the injury patterns. There are some suggestions of more than one episode but the patterns are not definitive. On some trees, there are stunted needles presumably on late secondary or adventitious candles. This may be the result of an insect or a pathogen or, maybe, an "acid rain" response. The only symptoms seen on species other than pine was a pattern suggesting sulfur dioxide on some oak (probably blackjack).

The effects of this single burn on the final yield of the plantation probably will not be measurable. Repeated episodes could result in measurable reductions in yield. However, such episodes do have a visual impact that can have a significant, adverse effect upon the public image of the Company.

One young pine on the southwest corner of the dike forming the cooling pond shows typical fluoride injury. Several small pines along the west side of the dike showed some symptoms that are probably fluoride injury.

The area is not readily accessible so that I was unable to examine the needles closely enough for confirmation. These are the only suggestions of effects from fluoride that I found in the area.

The types of vegetation and their distribution around the Swift Creek Mine area proposed for expansion are similar to those around the present operations. The effects from chronic sulfur dioxide exposure should be of no significance to the productivity of the area, assuming applicable emission and ambient air standards are met. The effect of fluorides should be as negligible as at present. Detectable symptoms may occasionally develop on sensitive material in the immediate vicinity of sources of gaseous fluorides.

Acute type injury on vegetation from sulfur dioxide, "acid mist", or both is an ever present hazard around sulfuric acid plants. Under steady operating conditions at either location, the probability of injury is very low. However, during start up and various temporary upsets or shifts in operations, emissions may be much greater than during steady operating conditions. These increased emissions increase the probability of injury. With the proper combination of meteorological conditions, duration of the excess emissions, time of year and a host of other environmental factors, a burn such as experienced along SR 137 is inevitable. Insofar as possible, changes in operations that increase emissions should be avoided during weather conditions favoring looping or coning plumes, sharp local inversions and prolonged stagnations.

Since farm crops are not an important use of the immediate area around the existing plant or the proposed expansion area, the economic impact of a single burn such as was experiended this year is low. However, more severe burns or the accumulative effect of repeated burns on the same area over several years can result in significant reduction in yield of the forest crop. I should point out that had the area along SR 137 been planted to a field crop such as corn, a significant crop loss would have occurred. Although a single moderate burn in a forest plantation may not result in any significant economic loss to the plantation, if it is highly visable to the public there will be an adverse effect on the Company image. From this standpoint, the area along SR 137 is especially vulnerable. A similar area along US 41 will be subject to a potentially greater impact from the proposed new installation.

As a matter of good public relations as well as protection against excessive claims, any burn suspected as a result of company operations should be investigated and documented as soon as detected. The limits of the affected area should be marked. General color photographs, as well as detailed closeup photographs of the various symptoms seen on all types of vegetation in the area, should be taken. Follow up surveys should be made at approximately weekly intervals, as needed, to document any changes in the symptoms or the extent of injury. Had this been done for this last burn, company staff might have been able to determine the specific meteorological and operating conditions that existed at the time, resulting in the injury. If I had had photographs of the early injury and subsequent development, I would have been able to provide a better statement of cause and a clearer evaluation of the other patterns now present. If a claim for damages had been made, such documentation would have been indispensible in limiting liability

Stafford Brandt

FIELD SURVEY

OCCIDENTAL CHEMICAL CO., White Springs, Fla.

March 28-29, 1978.

At the request of Sholtes and Koogler, Environmental Consultants, Gainesville, Fla., I examined the area around installations of Occidental Chemical Co., at White Springs, Fla., for possible injury to vegetation from air pollution.

For this visit, I followed the procedures used on previous visits over the past four years:

1. Examined various areas of pine plantations, hedge row deciduous material and any agricultural crops 10 to 20 miles from the plant site for background information on stage of growth, frequency of common diseases and general condition.
2. Tour the immediate area of the plant and surrounding mining areas with John Wester, of Occidental Chemical. Roads are usually available to give good coverage of the area out to 4-5 miles from the center of the site.
3. Using available county and other roads, tour the remaining area out to 8 to 10 miles from the center of the site.
4. Visit with other knowledgable observers of the area, if appropriate. On this visit, I talked with:
   a. Mr. Rance Andrews. Agricultural County Agent for Hamilton County, Fla.
   b. Mr. Eugene Schreiber, Forester, Owens Illinois.
   c. Mr. Charles Parrish, Forester, Continental Can Co.

The general appearance of the area is good. The pine are candling out well and are of good color. They show no clear evidence of any effects from the drought. As with previous surveys, I found no significant evidence of fluoride injury. A few pine on and beside the south and west dike forming the Number 1 cooling pond show a moderate degree of tip necrosis characteristic of fluoride accumulation. The observation is expected, considering the location. Maple, sweet gum, willow and other shrubby material along the dike do not show characteristic symptoms of fluoride injury. The nearest other pine, a few hundred yards away from the pond, appear normal.

Sometime last summer, possibly in July, an area of young pine along county route 137, due west of the chemical plant complex, were affected by something. I did not see the area until November. At that time, secondary infections and age had modified the symptoms. A short time exposure to a high concentration of SO_2, possibly with some acid mist, seems to be the most logical explanation. At that time the deciduous material was too old for any good confirmation. However, I could find no suggestions of fluoride injury. On this present trip the old injury is still evident but the trees are candling normally and damage, if any, will be slight. All deciduous material appears normal. Other than this one area, I have found no evidence of effects on vegetation from sulfur oxides.

Mr. Andrews had not seen or received any reports of possible air pollution effects on any agricultural crops during the past season. Since the pine along county route 137 belong to Owens Illinois, Mr. Schreiber had examined that area. He had not seen any other possible air pollution effects. Mr. Parrish had seen the effects along route 137 but no other effects on any of the pine in the area. Neither forester could give an accurate date of when he first saw the effect.

The area around the proposed expansion at the Swift Creek mine site is very similar to the present site. Fluorides should pose no more of a problem than at present. The major problem will probably be from sulfur oxides resulting from atypical operations during periods of atypical meteorology.

C. Stafford Brandt

CATTLE STUDY

HAMILTON COUNTY, FLORIDA

John B. Crum, D.V.M.

APRIL 1978

CATTLE STUDY - HAMILTON COUNTY, FLORIDA

This study is made for the purpose of determining if cattle born and raised near the phosphate mining and processing operations of Occidental Petroleum Company in North Florida are affected by air borne Fluorides that may or may not concentrate in the forage provided them.

The study occured in an area utilized primarily for the growing of pine trees. There are, however, a number of small farms and pasturelands located within a five mile radius of the plant. Owners of cattle located at varying distances and directions from the plant site were cooperative in offering and presenting their cattle for examination.

All cattle were raised on the premises on which they were examined unless otherwise noted. They had free access to pasture grasses year around and in some cases received locally grown hay and corn as a winter feed supplement.

No attempt was made to determine the possibility of Fluoride accumulation from drinking water sources, from pasture fertilization or mineral supplementation. It is doubtful in the opinion of the author that any of these sources have measurably contributed to concentrations that may exist.

An effort has been made to determine if individual animals had consumed excessive Fluorides during their early dentition periods (first five years of age) as evidenced by changes in the structure and wear of teeth. A classification for describing changes as they have occured in other studies throughout the country, and for the purpose of these evaluations is as follows:

0. Normal: smooth, translucent, glossy white enamel; tooth normal shovel shape.
1. Questionable effect: change discernible, exact cause not determined; may have enamel flecks: cavities if present may be unilateral or bilateral but with the absence of mottling.
2. Slight effect: slight mottling of enamel; may have slight staining but no wear; teeth normal shovel shape.
3. Moderate effect: definite mottling and staining of enamel; coarse mottling (large patches of chalky enamel); teeth may have slight signs of wear.
4. Marked effect: definite mottling, staining, and hypoplasia; may have pitting of enamel; definite wear of teeth; enamel may be pale cream color.
5. Excessive effect: definite erosion of enamel with excessive wear of teeth: staining and pitting of enamel may or may not be present.
8. Missing.
9. Deciduous tooth.

The number and percentage of individuals examined receiving a #2 (Slight Effect) or higher valuation are shown in the following chart:

Farm	Distance & Direction	Number Examined	Number with Dental Symptoms	%
Snell	$4\frac{1}{2}$ miles - South	8	0	0
Cristy	$5\frac{1}{2}$ miles - East	8	1	12.5%
Anderson	4 miles - S.W.	5	4	80%

The examinations revealed the cattle to be free from skeletal Fluorosis. There were a number of individuals demonstrating an early Fluorotic dental pattern indicating sufficient intake to cause staining and mottling of incisor teeth, but not sufficient to cause a loss of productivity at the present rate of intake.

John B. Crum

John B. Crum, D.V.M.

EXAMINATION OF ANIMALS FOR FLORIDE TOXICOSIS

Mr. Fred D. Cristy
Rt. 4 Box 85
Jasper, Florida

5½ miles East of Occidental Plant

Animal No.	Animal Identification	Photo No.	Lact Breed Grade (3)	Sex Age (2)	Incisors 1 2 3 4 (4)	Molars Extos Joint Stiff Flesh (5)	Where Raised (3)	Remarks
1	No I.D.		+ An G	F 10	0000	00000	Raised on Farm	
2	"		+ Ang G	F 7	0000	00000	"	
3	"		+ Ang G	F 8	2000	20000	"	uneven wear of molars
4	"		+ Ang G	F 8	0001	20000	"	"
5	"		+ Angx G	F. 10	0000	00000	"	Horned
6	"		N Ang Sh G	F 1	0000	00000	"	
7	"		+ Her Ang G	F 1	0000	00000	"	
8	"		+ Sh G	F 2	1010	00000	"	

EXAMINATION OF ANIMALS FOR FLORIDE TOXICOSIS

Mr. Jack Snell Facil, Florida	4½ miles South of Occidental Plant		Lact Breed Grade	Sex Age	Incisors 1 2 3 4	Molars Extos Joint Stiff Flesh	Where Raised	Remarks
Animal No.	Animal Identification	Photo No.	(3)	(2)	(4)	(5)	(3)	
1	No tag, no brand		N $\overset{\text{Her}}{\text{Ang}}$ G	F 5	1000	00000	on farm	
2	#85 Ear Tag		N $\overset{\text{Her}}{\text{Ang}}$ G	F 2½	0099	00000	"	
3	No I.D.		N $\overset{\text{Her}}{\text{Ang}}$ G	Steer 1	1199	00000	"	
4	Tattoo RE #$\overset{65}{\text{B}}$V5		+ Her G	F 13	0000	00000		Bought in 1967
5	No I.D.		+ Her G	F 5	0001	00000	On Farm	
6	#92 Ear Tag		N $\overset{\text{Her}}{\text{A}}$ G	F 2	0999	00000	"	
7	Tattoo $\overset{654}{\text{3V5}}$		+ Her G	F 13	0800	00000		Bought in 1967
8	No I.D.		+ Sh G	F 2	1010	00000	on farm	

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EXAMINATION OF ANIMALS FOR FLORIDE TOXICOSIS

Mr. Rufus Anderson Box 150 Genoa, Florida	4 miles S.W. of Occidental Plant		Lact Breed Grade	Sex Age	Incisors 1 2 3 4	Molars Extos Joint Stiff Flesh	Where Raised	Remarks
Animal No.	Animal Identification	Photo No.	(3)	(2)	(4)	(5)	(3)	
1	No I.D.		+ Ang G R poll	F 10	1100	0000Fair	On Farm	
2	"		+ Ang G	F $3\frac{1}{2}$	1228	2000Fair	"	
3	"		+ Poll Ang G	F 8	0012	1000Fair	"	
4	"		N Ang G	F $1\frac{1}{4}$	2111	0000Good	"	slight staining & chipping of enamel
5	"		N Ang G	F 10m	2111	0000Good	"	" (suckling)

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2.0 DIAMMONIUM PHSOPHATE PLANT SCRUBBER SYSTEM

2.1 Introduction

The information in this section is related to the scrubber system that New Wales is proposing to control particulate matter, ammonia and fluoride emissions from the reactor/granulator and the dryer of the proposed DAP plant. Included is a brief description of the process chemistry as it relates to air pollution control and an evaluation of various scrubber systems.

In specific response to request for additional information No. 2, contained in the EPA letter dated November 20, 1979, the reference in the Florida Air Pollution Construction Permit Application to "4/each bag collectors" is in error. There will be two bag collectors serving a common product cooler. This control system will be discussed further in Section 4.0 of this response.

2.2 Process Description

Diammonium phosphate is obtained by the reaction of ammonia with phosphoric acid. A flow diagram of the basic process is shown in Figure 2-1.

Anhydrous ammonia and phosphoric acid (about 40% P_2O_5) are reacted in a preneutralizer. The primary reaction is:

$$2\ NH_3 + H_3PO_4 \rightarrow (NH_4)_2\ HPO_4$$

The slurry thus produced flows into an ammoniator-granulator and is distributed over a bed of recycled fines. Ammoniation to the required mole ratio of 2.0 takes place in the granulator by injecting ammonia under the rolling bed of solids. It is necessary to feed excess ammonia to the granulator to achieve a 2.0 mole ratio. Excess ammonia and water vapor driven off by the heat of reaction are directed to a scrubber which uses phosphoric acid as the scrubbing liquid. The ammonia is almost completely recovered by the phosphoric acid scrubbing liquid and recycled to the preneutralizer.

Granulated diammonium phosphate is then sent to a dryer,and is then screened. Undersized and crushed oversized material are recycled to the granulator. Product sized material is cooled and sent to storage.

The sources of air pollutants in a DAP plant are identified in Figure 2-1. The sources include the reactor/granulator, the drier and the screens and cooler. Ammonia, SiF_4 and HF are emitted from the reactor/granulator. These same three pollutants plus particulate matter are emitted from the dryer and particulate matter only is emitted from the screens and cooler.

2.3 Scrubber Considerations

Because of the characteristics of the emissions from these three sources, New Wales proposes to use scrubbers to control the emissions from the reactor/granulator and dryer systems and a bag collector to control emissions from the cooler. The bag collector will be discussed in Section 4.0.

Emission control technology applied to DAP production serves three purposes: (1) recovery of ammonia; (2) recovery of particulate matter; and (3) prevention of emissions of ammonia, fluorides and particulate matter. Reactor/granulator emissions are vented directly to a wet scrubber system, while emissions from the dryer pass through cyclone collectors for product recovery and recycle before passing to a wet scrubber system.

Because of the multipurpose of the scrubber system, a dual system is used throughout the industry. There is a primary scrubber system designed to recover ammonia and particulate matter and a secondary system designed to control fluoride emissions.

The chemistry for ammonia recovery is identical to the process chemistry discussed earlier. Ammonia is scrubbed from offgases with excess phosphoric acid where it reacts to form ammonium phosphates which are retained in the scrubbing liquor. Particulate matter is also controlled with these scrubbers.

Equipment commonly used for primary scrubbing includes venturis and cyclonic spray towers. Primary scrubbers generally use 20 percent to 30 percent P_2O_5 phosphoric acid as scrubbing liquor principally to recover ammonia.

The common practice in industry is to use a venturi scrubber for the primary scrubbing system because of the efficiencies which can be obtained with these units, the fact that sprays are not necessary to distribute the phosphoric acid scrubbing liquor in the scrubber, and the fact that venturi scrubbers are self-cleaning.

With cyclonic scrubbers spray nozzles are required to distribute the scrubbing liquor in the scrubber. Because of impurities in the acid and the possibility of reaction products (ammonium phosphates, ammonium fluorosilicates and silicates) developing, the potential for nozzle plugging is very high. From a practical standpoint; therefore, cyclonic scrubbers have not been widely used.

The New Wales Chemical Company is proposing to use a coaxial venturi scrubber. A schematic diagram of one of these scrubbers is presented as Figure 2-2.

The coaxial venturi scrubber gets its name from the fact that it is a cylindrical scrubber with the separator constructed concentrically around the venturi. The scrubbing liquor is flooded into the throat and atomization occurs as a result of the velocity of the gas passing through the throat. The scrubber will operate at a pressure drop in the range of 12 to 14 inches of water. As stated previously, the primary function of this scrubber is to remove and recover ammonia and particulate matter prior to the gases passing into a tail gas scrubber for fluoride control.

Fluorides are scrubbed from offgases in the secondary scrubbing system according to the reactions:

$$2HF\uparrow + SiF_4\uparrow \rightleftarrows H_2SiF_6. + \Delta$$

High temperature tends to increase the vapor pressure at both HF and SiF_4 in the HF-SiF_4-scrubber water system and, hence drive the reaction to the left. These vapor pressures set the lower limit of concentration in the gas phase leaving the scrubber.

In addition to the reactions given, hydrolysis of SiF_4 occurs when the concentration of this component is higher than the vapor pressure equilibrium values, according to:

$$3SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6$$

This reaction tends to occur as the temperature of a gas stream is reduced in the presence of water, or the pH of the water is increased. This leads to the formation of gelatinous deposits of polymeric silica which tend to plug scrubber packings. The types of scrubbers which are likely to perform well in this service are:

(1) Spray sections
(2) Wet cyclonic scrubbers
(3) Venturi scrubbers
(4) Packed scrubbers

Spray sections are not capable of the high efficiencies required for compliance with present regulations. They may; however, be useful as a preconditioner to cool the gas stream and remove fluorides at relatively high concentration levels. They have relatively little pressure drop and can be used to bring large volumes of pond water into contact with the gas to reduce the temperature and improve the absorption equilibrium.

Wet cyclones are also limited in efficiency, but may be used as precoolers. They have a higher pressure drop requirement at high liquid flows than do the spray chambers and are therefore not commonly used.

Venturi scrubbers can bring about effective contact and gas absorption when sufficient energy is imparted to the gas to atomize the scrubbing liquor and create very small droplets. The contact time in a venturi is very short, and it has been found that the power requirements at a given level of fluoride absorption are high as compared with packed scrubbers.

The spray packed bed scrubber is the most commonly used scrubber for fluoride control. These scrubbers consist of two sections--a spray chamber and a packed bed. Both spray and packed sections are equipped with a gas inlet. Effluent streams with relatively high fluoride concentrations--particularly those rich in silicon tetrafluoride--are treated in the spray chamber before entering the packing. This preliminary scrubbing removes silicon tetrafluoride, thereby minimizing bed plugging. It also reduces packed stage loading and provides some solids handling capacity.

The spray section consists of a series of counter-current spray manifolds followed by a system of irrigated baffles or a dewatering section. The baffles or dewatering section remove precipitated silica and prevent the formation of scale in the spray chamber and plugging of the packed section.

Counter-current packed scrubbers have an inherent advantage over concurrent or cross-flow scrubbers for gas absorption applications where the concentration of contaminant leaving the scrubber approaches equilibrium with the scrubbing liquor. This advantage is most clearly explained by reference to Figure 2-3.

Here the concentration of contaminant in the gas phase is plotted as a function of position in the scrubber. Y_1 represents the inlet concentration and Y_2 the outlet concentration. In a counter-current scrubber, the liquor contains some of the contaminant and has a composition such that gas in equilibrium with it would have a concentration Y_2' at the gas outlet, and Y_1' at the gas inlet. The difference between Y and Y' at any point in the scrubber is the absorption driving force.

The counter-current scrubber has the highest potential removal efficiency, because it contacts the gas leaving the scrubber with the cleanest scrubbing liquor.

The concurrent scrubber does just the opposite and tends to bring the discharge gas into equilibrium with the most contaminated liquor. However, the concurrent scrubbers are considerably less prone to plugging with solids than the counter-current, and also require less gas pressure drop to operate.

The cross-flow scrubber is a compromise between the counter-current and concurrent flow scrubbers. With these scrubbers the gas flow is horizontal through the scrubber with water being sprayed on the top of the packing and flowing vertically through the scrubber. There is an increase in the fluoride concentration of the scrubber water as it passes from the top to the bottom of the scrubber. This gradient is essentially constant throughout the length of the packing. This results in the flat vapor pressure curve for the scrubber water in a cross-flow scrubber as shown in Figure 2-3.

Theoretically, it is the fluoride vapor pressure over pond water at the exit of the packing in a tail gas scrubber that establishes the minimum fluoride concentration that can be achieved by scrubbing. The degree to which this concentration is approached depends upon the number of transfer units designed into a scrubber. In the case of New Wales, approximately six to seven transfer units are designed into the tail gas scrubbers. This will be adequate to meet New Source Performance Standards which is the requirement for fluoride control in the sources proposed by

New Wales. The New Source Performance Standards are the limiting standards since the total actual fluoride emission increase will be less than 50 tons per year.

2.4 Summary

The overall scrubbing system, consisting of the primary scrubber and the secondary scrubber, in the DAP plant must be designed with Best Available Control Technology for particulate matter in mind since the actual increase in particulate matter emissions resulting from the proposed expansion will exceed 50 tons per year. As previously discussed in this section, the primary scrubbing system - the coaxial venturi scrubber - was designed to reduce the concentration of particulate matter emissions in the gas stream to approximately 0.01 grains per standard cubic foot, dry. This scrubber was also designed to remove and recover ammonia. The secondary scrubber - the packed bed scrubber - was designed to remove fluorides from the tail gas stream before the gas stream is exhausted to the atmosphere. As discussed; however, there is a reaction that creates particulate matter [$(Si(OH)_2$ and SiO_2] within the tail gas scrubber. This particulate matter causes the packing to plug and is responsible for a periodic shut down of the DAP plant for scrubber cleaning.

In addition to plugging the tail gas scrubber, some of this particulate matter breaks through the scrubber and increases the particulate matter concentration in the tail gas stream being exhausted to the atmosphere to a maximum of 0.02 grains per standard cubic foot, dry. It should be noted that this maximum concentration will occur just prior to the shutdown of the scrubber for cleaning. Immediately after cleaning the particulate matter concentration in the tail gas stream will approach

0.01 grains per standard cubic foot, dry. This concentration will then increase to the 0.02 grains per standard cubic foot, dry as the packing plugs.

As reported herein, the plugging of the tail gas scrubber is due to the formation of silicon hydroxide and silicon dioxide. Both occur as levels of SiF_4 in the tail gas stream exceed equilibrium concentrations. This occurs when the temperature of the tail gas stream is reduced or when the pH of the scrubber water increases. The latter would occur when ammonia breaks through the primary scrubber as a result of slight upsets in plant operating conditions.

To summarize the control of air pollutant emissions from the reactor/granulator and dryer it can be stated that the particulate matter and ammonia are well controlled by the primary scrubbing system and that fluorides are well controlled by the packed secondary scrubber. The problem inherent with DAP scrubbing systems is the formation of silicon compounds in the packed secondary scrubber which cause scrubber plugging and increase the concentration of particulate matter in the tail gas stream. The effectiveness of the overall scrubbing system; therefore, depends upon the design and operation of the tail gas scrubber in a manner that will reduce the effects of the silicon compounds. Both the design and the operation are more dependent upon experience than theory.

2.5 Proposed New Wales DAP Scrubber System

In view of the above considerations, experience New Wales has had with their existing DAP plant and experience other phosphate fertilizer companies have had with other control systems, New Wales is proposing the following control system:

1. A coaxial venturi scrubber - separator operating at 12 to 14 inches of water pressure drop to control ammonia and particulate matter emissions from the reactor/granulators. There will be two such scrubbers, one for each of the two identical reactor/granulator systems.

2. Identical coaxial venturi scrubber - separators will be used to control ammonia and particulate matter emissions from the two identical dryers.

3. Counter-current flow packed tail gas scrubbers will follow each of the venturi scrubbers for fluoride control. Each of the packed scrubbers will be preceded by a spray chamber to precondition the gas. The spray chamber will reduce the temperature of the gas stream, reduce to some extent the fluoride level in the gas stream and provide some capability for particulate matter control. The pond water introduced in the spray chamber will be removed in a dewatering section at the base of the tail gas scrubber. The dewatering section will consist of a section of scrubber shell containing no packing. The gas velocity in this section will be low enough to permit the separation of water droplets and precipitated silicon compounds from the gas stream before the gas stream enters the packing.

   The gas stream will then pass through the packed section counter-current to pond water introduced at the top of the packing. Mist eliminators will follow the packing section to eliminate water droplets prior to the tail gas being discharged to the atmosphere.

The venturi scrubbers were selected because of the particulate matter and ammonia removal efficiencies which can be obtained with these scrubbers. The venturi scrubber is also self-cleaning and the fact that spray nozzles are not required to distribute the scrubbing liquor in the scrubber eliminates another potential operational problem.

The counter-current flow tail gas scrubber was selected because it can effectively reduce fluoride emissions required by New Source Performance Standards with a minimum pressure drop. The counter-current design was selected because recent applications of this type scrubber within the industry have proved to have fewer operating problems than the conventional cross-flow packed scrubber. One serious problem with cross-flow packed scrubbers is the potential for a void to develop at the top of the packing as the packing settles. This problem is magnified by the fact that the packing has to be removed periodically for cleaning. The use of a counter-current flow scrubber minimizes the chance of voids in the packing and hence the channeling of tail gas through the scrubber.

The particulate matter concentration in the tail gas stream that New Wales is proposing as Best Available Control Technology, taking into consideration all of the aforementioned factors, is 0.02 grains per standard cubic foot, dry. The fluoride concentration in the tail gas stream will satisfy New Source Performance Standards of 0.06 pounds of fluoride emitted per ton of P_2O_5 input to the plant.

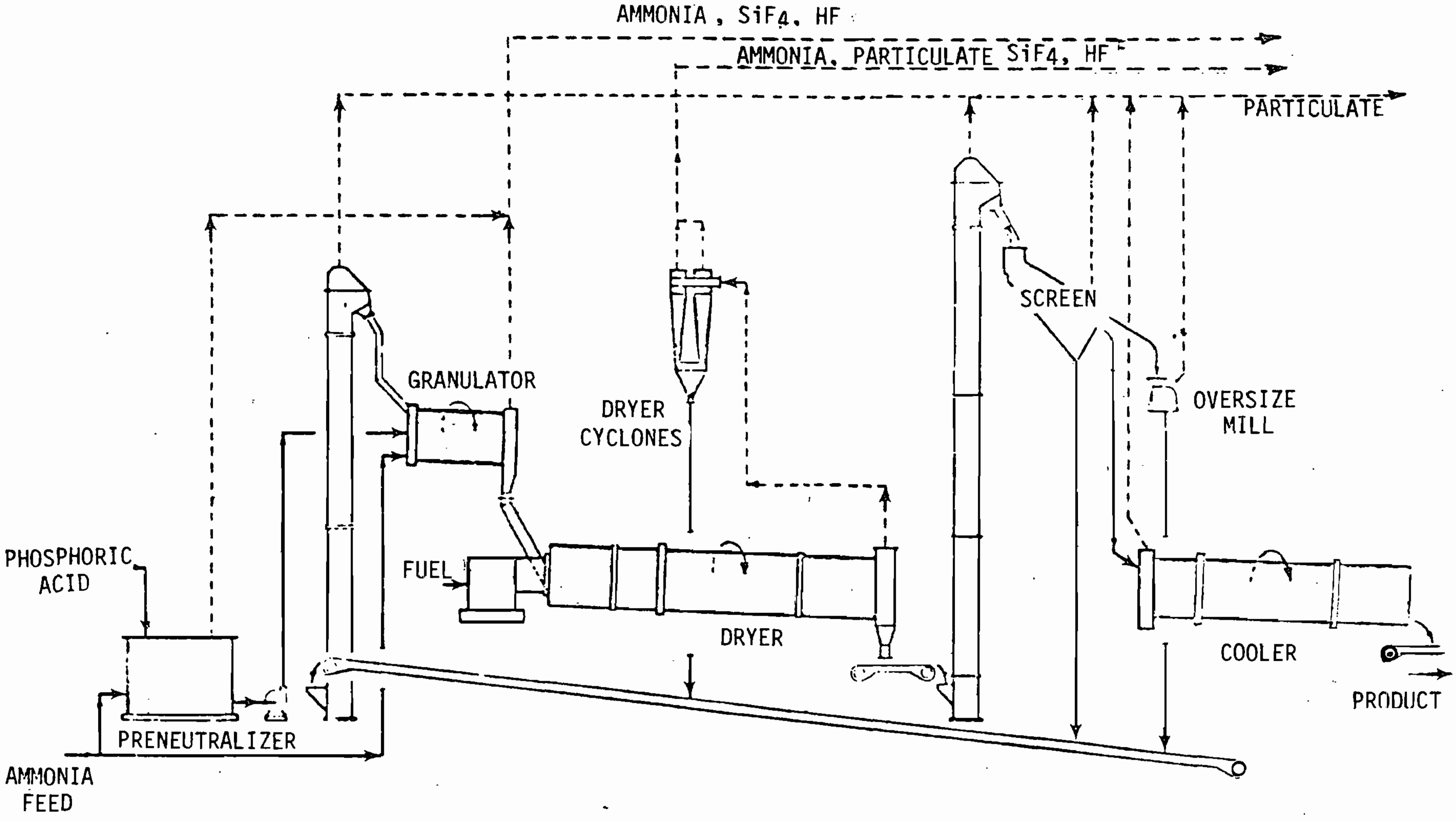


FIGURE 2-1 DIAMMONIUM PHOSPHATE PROCESS

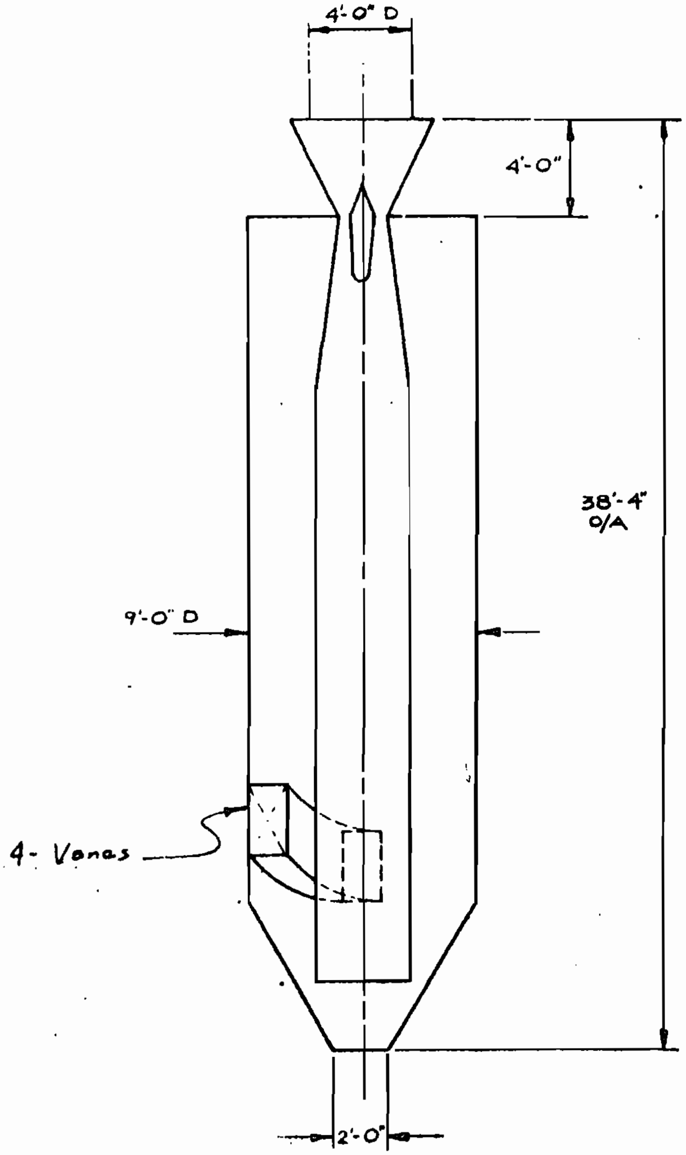


FIGURE 2-2

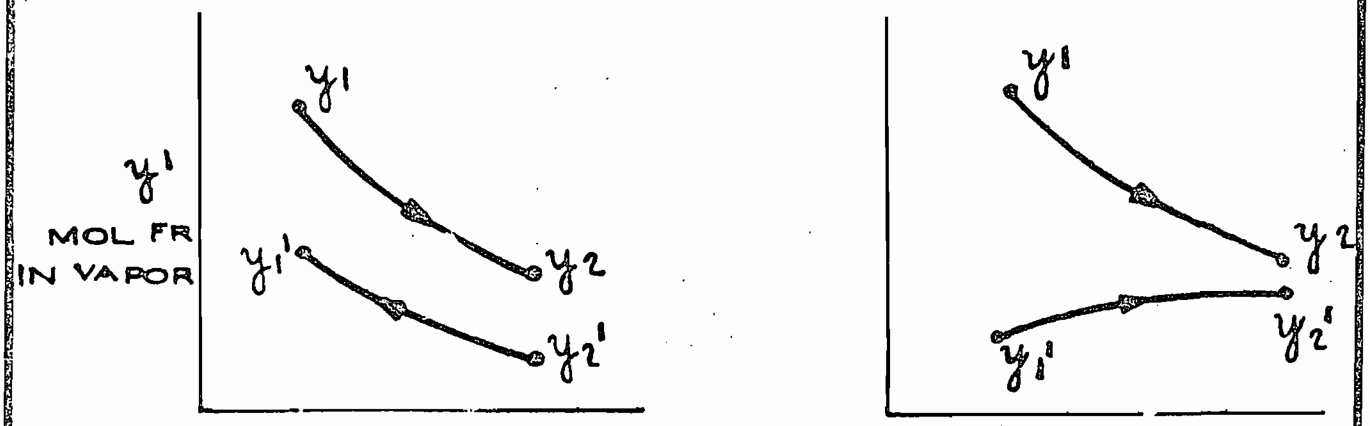
COAXIAL VENTURI SCRUBBER

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

FIGURE 2-3

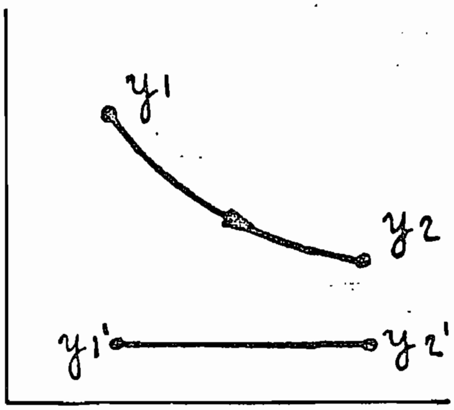
COMPARISON OF SCRUBBER TYPES

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA



a. COUNTER CURRENT SCRUBBER

b. CON-CURRENT SCRUBBER



C. CROSS FLOW SCRUBBER

3.0 WET PHOSPHORIC ACID PLANT SCRUBBER SYSTEM

3.1 Introduction

The increase in actual fluoride emissions as a result of the proposed New Wales expansion will be less than 50 tons per year. As a result of this fluoride emissions will be controlled to meet New Source Performance Standards. BACT will not have to be employed.

The purpose of this section therefore, is to respond to a specific request addressed in the EPA letter of November 20, 1979 and to provide the permit reviewer with a brief description of wet process phosphoric acid production.

The description of the production process will lead into the justification of the scrubber system proposed by New Wales. This in turn will lead to a response to a specific question posed by EPA.

3.2 Process Description

The most common method of producing phosphoric acid is by a wet process utilizing sulfuric acid. A flow diagram of this process is presented as Figure 3-1. The use of this process is the reason for the existence of the gypsum stack.

Phosphate rock is a complex material; the principal mineral constituent, fluorapatite, contains calcium, phosphate, fluoride carbonate and many other elements or groups bound together in a crystal lattice. When the rock is treated with a strong mineral acid, the apatite lattice is destroyed and the phosphate constituent is converted to phosphoric acid. The overall reactions with sulfuric acid are:

the tricalcium phosphate constituent is converted to phosphoric acid and calcium sulfate

$$Ca_3(PO_4)_2 + H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4,$$

the calcium fluoride constituent of the fluorapatite reacts with sulfuric acid to produce hydrogen fluoride and calcium sulfate

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4, \text{ and}$$

the calcium carbonate constituent is converted to carbon dioxide and calcium sulfate

$$Ca\overset{C}{\cancel{S}}O_3 + H_2SO_4 \rightarrow CO_2 + CaSO_4 + H_2O.$$

The excess fluoride present in the phosphate rock also reacts with phosphoric acid to form HF.

$$CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HF$$

Then HF reacts with excess silica:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

During the acid concentration steps a considerable portion of the fluosilicic acid dissociates to form HF and SiF_4:

$$H_2SiF_6 \rightleftarrows SiF_4 + 2HF$$

The fumes resulting from H_2SiF_6 volatilization are scrubbed with water; however, regenerating the H_2SiF_6:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

which is pumped to the ponds with the gypsum slurry.

3.3 Sources of Gaseous Fluorides

Fluoride emissions from wet process acid manufacture are gaseous silicon tetrafluoride and hydrogen fluoride. The reactor is the major source of fluoride emissions from the process, accounting for as much as

90 percent of the fluorides emitted from an uncontrolled plant. Additional sources are the filter, the filtrate feed and the acid storage tanks. Fluoride emissions will vary depending upon the type of rock treated and the process used.

Modern reactors emit fluorides from two sources; the reaction vessel and the vacuum flash cooler. The primary source is the reactor tank, where silicon tetrafluoride and hydrogen fluoride are evolved during the digestion of the phosphate rock.

To prevent an excessive temperature rise in the reactor, the heat of reaction is removed by cycling a portion of the reaction slurry through a vacuum flash cooler. Vapors from the cooler are condensed in a barometric condenser and sent to a hot well while the noncondensables are removed by a steam ejector and also discharged to the hot well. This arrangement is illustrated in Figure 3-1. The fluorides evolved in the flash cooler are absorbed by the cooling water in the barometric condenser and subsequently discharged to the cooling pond. There is no vent in the seal tank and, hence, no release of gaseous fluorides.

The filter is the second largest source of fluoride emissions. Most of the fluorides are evolved at the points where feed acid and wash liquor are introduced to the filter. These locations are hooded and vented to the digester scrubber.

A potential source of fluoride emissions is the multiple effect evaporator used to concentrate the phosphoric acid from 30 percent P_2O_5 to 54 percent P_2O_5. It has been estimated that 20 to 40 percent of the fluoride originally introduced into the process with the rock is vaporized during this operation. These fluorides are collected in the barometric condensers or exit with the noncondensables which are sent to the hot well and then to the cooling pond. The hot well is not vented and is therefore, not a source of gaseous fluorides.

In addition to the preceding sources of fluoride emissions, there are several minor sources. These include the vents from such points as sumps, clarifiers and acid tanks. Collectively, these sources of fluoride emissions can be significant and will be ducted to the plant scrubber.

Table 3-1 illustrates a typical material balance for the fluoride originally present in phosphate rock. It should be noted that the results in any given wet process plant may differ considerably from those shown in the table. Fluoride distribution will depend upon the type of rock treated, process used and kind of operation prevailing.

TABLE 3-1

TYPICAL MATERIAL BALANCE OF FLUORIDE IN MANUFACTURE OF WET-PROCESS PHOSPHORIC ACID

Fluoride Input	# F/100 # Feed Rock
Feed	3.9
Fluoride Output	**# F/100 # Feed Rock**
Product acid	1.0 (26%)
Gypsum	1.2 (31%)
Barometric condensers	1.67 (43%)
Air	0.03 (<1%)
TOTAL	3.9 (100%)

Fluoride-bearing water from the barometric condensers and hotwell as well as the gypsum slurry is sent to the pond/stack. Potential fluoride emissions from the pond/stack are discussed in Section 1.0.

3.4 Proposed New Wales WPPA Scrubber System

Since New Wales is proposing to feed wet rock to the phosphoric acid plant, particulate matter emissions will be eliminated(1). The only potential pollutant from this source will, therefore, be fluoride compounds.

Of the available types of pollution control, wet scrubbers have been the exclusive choice for treatment of contaminated process vapors generated in the digester and filter. Problems in scrubber efficiency result from deposition of hydrated silica within water nozzles or scrubber packing, which affects liquid-vapor contact.

Cross-flow packed scrubbers provided high absorption capabilities and tend to operate free from plugging when preceded by a spray section. When gases enter the spray section, hot vapors are cooled, high concentrations of fluorides are reduced and reaction takes place between the water and silicon tetrafluoride in the gas.

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

The silica (SiO_2) precipitates in the form of a hydrated gel [$Si(OH)_4$].

$$SiO_2 + 2H_2O \rightarrow Si(OH)_4$$

When fluoride loading is substantially reduced, gas passes through the more efficient stage, a cross-flow packed scrubber, where the remaining hydrogen fluoride is removed. The cross-flow design, with scrubbing spray normal to the direction of the gas flow, washes precipitates off the packing to prevent plugging. The collected deposits are near the front of the packed bed, which is more heavily irrigated to reduce solids build-up.

Although venturi scrubbers provide effective contact and gas absorption, they have a major disadvantage in that a high pressure drop and corresponding high energy requirement are necessary to meet the given standards for emissions.

Important factors observed in efficiencies of control devices are composition and temperature of scrubbing water and the build-up of solids (silica compounds) in the scrubber. The cross-flow packed scrubber has proven effective in controlling fluoride emissions from the existing New Wales phosphoric acid plants. These existing plants meet NSPS (0.01 pounds fluoride per ton P_2O_5) and there is no reason to expect that the scrubber system proposed for the new plant will not.

0.02

If additional fluoride removal was required the most effective way to accomplish this would be to place additional packing in the packed scrubber (i.e., increase the number of transfer units in the packed scrubber) rather than to place a venturi scrubber in line with the cross-flow packed scrubber as suggested in the EPA letter of November 20, 1979.

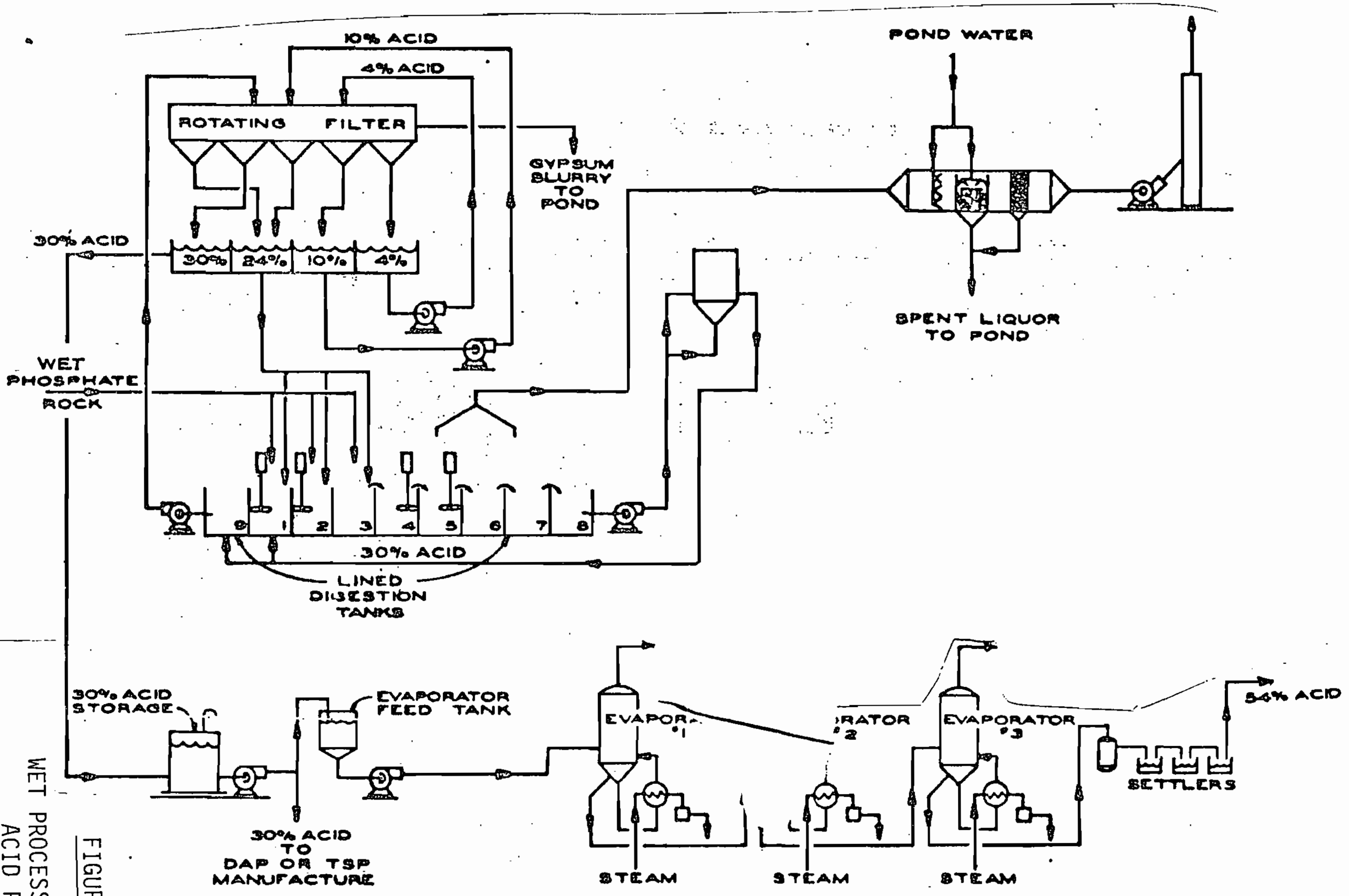


FIGURE 3-1

WET PROCESS PHOSPHORIC ACID PROCESS

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

SHOLTES & KOOGLER

REFERENCES
SECTION 3

1. Draft Areawide Environmental Impact Statement, Central Florida Phosphate Industry, EPA 904/9-78-006, USEPA, Region IV, Atlanta, Georgia, March 1978.

4.0 DIAMMONIUM PHOSPHATE PLANT BAG COLLECTOR

As discussed in Section 2.0, the air pollutant emissions from a DAP plant consist of ammonia and fluorides from the reactor/granulator system, ammonia, fluorides and particulate matter from the dryer system and particulate matter only from the cooler.

New Wales has selected scrubber systems to control the multiple emissions from the reactor/granulator and dryer systems as discussed in Section 2.0. A bag collector is proposed to control the emissions from the cooler since only particulate matter is emitted from this source.

The fertilizer diammonium phosphate (DAP) consists of two moles of ammonia for each mole of P_2O_5, hence the name DAP. In order to obtain this mole ratio excess ammonia must be added to the system. This excess ammonia reacts with and neutralizes all of the phosphoric acid, the free sulfuric acid and the free fluoride acids (HF and H_2SiF_6). The resulting product therefore has a pH of approximately 7.2.

Because of the neutralization of all of the acids and in particular the fluoride acids, there is no chance for gaseous fluoride compounds to evolve from the DAP product. As a result of this there are no gaseous fluoride emissions from the DAP cooler nor from the DAP storage building.

Since there are only particulate matter emissions from the DAP cooler, it is the opinion of New Wales that BACT for the particulate matter would be a bag collector. With a bag collector the particulate matter concentration in the tail gas stream from the cooler can be reduced to 0.01 grains per standard cubic foot, dry.

If a scrubber were used for the particulate matter control, the gas stream would be brought into intimate contact with pond water. Since the pond water contains approximately 8500 ppm of fluoride at New Wales, some of this fluoride would be stripped from the water and introduced to the gas stream. This would create a source of fluoride emissions where none had previously existed. Furthermore, the particulate matter concentration in the gas stream cannot be significantly reduced below 0.01 grains per standard cubic foot with a scrubber. Therefore, there is no advantage to be gained by considering a scrubber; only the disadvantage of adding fluorides to a gas stream previously free of fluorides.

Based on these considerations a bag collector is proposed as BACT for reducing particulate matter emissions from the DAP plant product cooler.

5.0 CONTROL OF FLUORIDE EMISSIONS FROM PROPOSED PHOSPHORIC ACID PLANT

The chemistry resulting in the generation of gaseous fluoride compounds during the production of wet process phosphoric acid is discussed in Section 3.0.

Gaseous fluoride compounds are generated and evolve from the digester, from the filter and from several minor sources throughout the plant. All of these sources will be vented and discharged through the cross-flow packed scrubber described in Section 3.0.

Evaporator and condenser water discharged to the seal tanks and hot well will also contain a considerable amount of fluorides. Neither the seal tank nor the hot well will be vented however, and will therefore, not constitute a source of gaseous fluoride emissions. The water contained in the seal tank and hot well will be discharged to the cooling pond. Fluoride emissions from cooling pond and gypsum stacks were discussed in Section 1.0 of this response.

6.0 CONTROL OF FLUORIDE EMISSIONS FROM COOLING PONDS

In Item 6, Additional Information Requirements, November 20, 1979, a request for a BACT analysis for fluoride emissions from cooling ponds was made. The magnitude of fluoride emissions from the cooling ponds was discussed in Section 1.0. It was concluded that the total actual fluoride emission increase resulting from the proposed expansion at New Wales will be less than 50 tons per year and therefore BACT will not apply to fluoride emissions.

In spite of this, a brief discussion of alternatives for controlling fluoride emissions from cooling ponds was presented in Section 1.0.

It was concluded that fluoride recovery from seal tank and hot well water will not affect fluoride emissions from cooling ponds. It was determined that liming would be quite effective for reducing fluoride emissions; however, the increase in particulate matter, sulfur dioxide and nitrogen oxides emissions from handling, calcining and slaking the lime would more than offset the reduction in fluoride emissions. In addition to air pollution considerations there would be a considerable consumption of fuel oil required to calcine the lime.

Other alternatives such as process modifications were evaluated and determined not to be effective.

7.0 FUEL RELATED AIR POLLUTANT EMISSIONS IN THE DAP PLANT

7.1 Introduction

Heat is required in the DAP product dryer to remove excess water from the product. New Wales is designing the dryers to use fuel oil combustion for the heat source.

For design purposes it is assumed that two gallons of fuel oil will be required to dry one ton of product. The rated production capacity of the proposed DAP plant is 140 tons per hour total (70 tons per hour in each of two identical trains). This production rate will require a maximum of 280 gallons per hour of fuel oil. New Wales is proposing to use a residual No. 6 fuel oil with a maximum 2.5 percent sulfur content.

7.2 SO_2 Emissions

Since there is free ammonia in the product entering the dryer, it is expected that sulfur dioxide will be partially absorbed by a reaction with the ammonia. New Wales has conducted emission measurements and can commit to a maximum sulfur dioxide emission rate from the total DAP plant of 44 pounds per hour. This will be a maximum SO_2 emission rate of 22 pounds per hour from each of the two dryers.

This commitment is equivalent to a 60 percent reduction in the SO_2 emission rate with the dryers burning a 2.5 percent sulfur fuel at a combined rate of 280 gallons per hour. This is also equivalent to burning a fuel oil with 1.0 percent sulfur.

This commitment will reduce the actual sulfur dioxide emissions from the DAP plant from 457 tons per year to 183 tons per year which is only four percent of the total sulfur dioxide emissions from the "new sources" at the New Wales Chemical Complex. Because of the SO_2 sorption capacity inherent with the DAP process the combustion of fuel with a 2.5 percent sulfur is equivalent to using a 1.0 percent sulfur fuel. No expenditure of energy is required to achieve the sorption and the SO_2 remaining in the tail gas has been shown not to cause or contribute to a violation of secondary air quality standards or PSD increments. Because of these factors the use of a 2.5 percent sulfur fuel is considered BACT.

7.3 NO_x Emissions

The combination of fuel oil in the DAP dryer will generate some NO_x as a result of the oxidation of atmospheric nitrogen at the peak temperatures achieved in the flame. The quantity of NO_x generated is expected to be low; however, because of the nature of the dryer performance.

The purpose of the burner in the DAP dryer is to heat and which in turn is used to drive excess moisture from the granular DAP product. If the temperature is too high the DAP will decompose. This performance differs from that of a boiler where the intent is to transfer the heat of combustion to water. The latter requires as little excess combustion air as possible since the heat transferred to the excess air is lost.

In a DAP dryer burner the heavy fuel oil is steam atomized. Additionally about 150 percent stoichiometric combustion air (50 percent excess air) is fed through the burner. Downstream of the burner nozzle quench air is added resulting in a total air flow equivalent to 300-500 percent excess air.

The use of steam atomization of the fuel and the addition of quench air results in a burner that functions much like a low NO_x burner(1). The addition of less than 50 percent excess air at the burner would probably result in lower NO_x emissions but it would also result in higher temperatures in the front of the kiln which in turn would cause DAP decomposition.

Because of the nature of the drying operation the DAP burner functions much like a low NO_x burner. Further modification of the burner to reduce NO_x emissions, such as by reducing primary combustion air is not possible. Temperatures resulting from the reduction in primary air would cause an increase in temperature at the end of the dryer that would cause product decomposition. Flue gas recirculation, likewise is not feasible because of the high excess air flow used in the dryer. The flue gas has an oxygen content not significantly lower than that of air.

It is the opinion of New Wales and the burner supplier (John Zink, Inc.) that the burners used in DAP plants represent BACT for NO_x control in this type source.

In response to a specific EPA request for information, the air flow to the burner and the quench air orifices is controlled by fixed orifices in the air line. The fuel flow rate is controlled by an orifice and the pressure of the oil pump.

REFERENCES
SECTION 7

1. Personal communication with Lee Massey, John Zink, Inc., Tulsa, Oklahoma, December 7, 1979.

8.0 CO EMISSIONS

Potential CO emissions could result from the combustion of fuel oil in the DAP plant dryer and by the combustion of the 0.25 percent petroleum residue in the sulfur burned in the sulfuric acid plants. In both cases it was assumed that EPA emission factors would apply and a CO emission rate of 6.5 tons per year was calculated (Attachment 1). Pollutants emitted at this rate are exempt from review under current PSD regulations.

ATTACHMENT 1

CALCULATION OF POTENTIAL AND ACTUAL EMISSIONS

CARBON MONOXIDE

DAP Plant

Oil Consumption in Dryers (2 dryers @ 70 TPH each)

$$2 \times 70 \frac{\text{tons DAP}}{\text{hour}} \times 2 \frac{\text{gal oil}}{\text{ton DAP}} = 280 \text{ gal/hour}$$

CO emission factor - 5 lb/1000 gal (AP-42 sup 7)

CO = 280/1000 × 5 × 8760 × 0.95 × 1/2000

= 5.8 tons/year (Potential & Actual)

H_2SO_4 Plant

Two plants at 2000 TPD H_2SO_4

Operating factor = 0.95

Sulfur consumption at 0.33 tons/ton acid

= 2000 × 2 × 0.33 × 2000 lb/ton

= 2.664×10^6 lb/day

Petroleum content of dark sulfur = 0.25%

Equivalent Petroleum Consumption

= $2.664 \times 10^6 \times 0.25/100 \times 1/8$ lb/gal

= 833 gal/day

CO emission factor = 5 lb/1000 gal (AP-42/7)

CO = 833/1000 × 5 × 365 × 0.95 × 1/2000

= 0.7 tons/yr (Potential & Actual)

TOTAL CO Emission

= 5.8+0.7 = $\boxed{\text{6.5 ton/yr Potential \& Actual}}$

9.0 DOWNWASH ANALYSIS

When pollutants are emitted from a stack or vent at a velocity less than two times the prevailing wind speed or at a height less than approximately 2.5 times the height of the nearby structures, there is a possibility that the pollutant will be entrapped in the turbulent wake generated by the structure or stack and be mixed immediately to ground level. Such an event is referred to as a downwash.

This section includes an analysis of downwash on air quality for the various sources proposed by New Wales.

The sulfuric acid plants proposed by New Wales will have 200 foot high stacks. The highest structure associated with the sulfuric acid plants or near these plants will be approximately 86 feet high. The 200 foot stack is 2.33 times higher than this structure. In addition, the tail gas velocity exiting the stack will be approximately 10.8 meters per second; approximately three times the average wind speed at the New Wales site. Considering the height of the sulfuric acid plant stack relative to surrounding structures and the tail gas velocity leaving the stack, it is very unlikely that downwash from these sources will occur.

The three stacks exhausting the DAP plant and the two stacks exhausting the third product load-out system are all less than two times the height of nearby structures. Because of this, a downwash analysis has been made for particulate matter and sulfur dioxide emitted from these sources. The analysis was conducted after a method suggested by Turner(1). Turner suggests that the initial σ_z be equal to the structure height divided by 2.1 and that the initial σ_y be equal to the structure width divided by 4.3.

For the analysis described herein "structure height" has been defined as the stack height. This is assumed to be reasonable since the pollutant will be initially mixed between the top of the stack and ground level. In the case of the horizontal dispersion the "structure width" is assumed to be twice the stack height. This dimension was selected since the structures adjacent to the stacks being considered are much broader than the stack is high. This is apparent from viewing a plot plan of the New Wales Chemical Complex. From a practical point of view; however, it was not considered reasonable that the pollutant would initially be dispersed over the total breadth of adjacent structures. For purposes of this analysis; therefore, the structure width was assumed to be equal to twice the stack height.

One additional assumption is that the stability of the atmosphere would become one stability class less stable during downwash conditions to represent the mechanically induced turbulence that would exist at the ground surface. This mechanical turbulence would result from the wind passing over and around structures on the New Wales plant site and trees immediately off the plant site. It would act to disperse the downwashed pollutant at a greater rate near the ground surface than the rate at which the pollutant would be dispersed under normal dispersion conditions. The increased instability is reasonable since the average wind speed for the conditions evaluated averaged 10 miles per hour for the 24-hour period. This wind speed will certainly generate mechanical turbulence in the air mass at the ground surface.

Another assumption made was that downwash would occur for the entire 24-hour period or 3-hour period. Observation of sources similar to those proposed by New Wales has shown that downwash occurs very infrequently and certainly not for periods of 24 hours as assumed in this analysis. This assumption; therefore, will result in a conservatively high downwash impact for the 24-hour periods.

The downwash analysis was conducted with the air quality model PAL. In each case analyzed the air quality impact of the source was determined assuming normal dispersion patterns and again assuming that downwash would occur. The meteorological data input to the model were the data resulting in the maximum impact from the DAP plant as determined with the CRSTER air quality model. Receptor distances were established to equal distances to the points of maximum impact as determined by the previous modeling and to represent distances to the nearest New Wales property line.

The specific conditions evaluated for downwash impact include particulate matter emissions from the DAP plant, particulate matter emissions from the third product load-out and sulfur dioxide emissions from the DAP plant. The results of these analyses are summarized in Table 9-1. It can be seen that at the point where the maximum 24-hour impact of emissions from the DAP plant are expected to occur under normal dispersion conditions (1.1 km from the source) the impact under downwash conditions will be 30-50 percent higher. The 24-hour particulate matter impact under downwash conditions is 13 ug/m^3 compared to 10 ug/m^3 under normal dispersion conditions and the downwash SO_2 impact is 15 ug/m^3

compared with 10 ug/m^3 under normal conditions. At the nearest property line distance (1.9 km from the source), the 24-hour impacts of both particulate matter and SO_2 are less under downwash conditions than under normal dispersion conditions.

The maximum 3-hour SO_2 impact from the DAP plant under normal dispersion conditions occurs at 1.1 km from the source. At this distance the SO_2 impact under downwash conditions is 31 ug/m^3 compared with 43 ug/m^3 under normal dispersion conditions. At the nearest property line distance (1.9 km) and at the distance where the maximum 3-hour SO_2 impact from all sources occurs (2.5+ km), the 3-hour SO_2 impact under downwash conditions is also less than the impact under normal dispersion conditions.

The impact of particulate matter emissions from the third product load-out at all distances beyond 0.5 km is greater under normal dispersion conditions than under downwash conditions.

If the increased impact in particulate matter and/or sulfur dioxide emissions resulting from downwash conditions are added to the impacts summarized in Figures 5-3 and 5-7 of the information document submitted on October 19, 1979, the resulting pollutant levels at the points of maximum impact will still not threaten ambient air quality standards nor PSD increments. At property line distances the impacts of emissions under downwash conditions will be less than under normal dispersion conditions.

TABLE 9-1

DOWNWASH ANALYSES OF POLLUTANTS EMITTED FROM PROPOSED DAP PLANT AND THIRD PRODUCT LOAD-OUT

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

Source/Pollutant	Receptor Distance from Source (km)	24-Hour Groundlevel Pollutant Concentration Normal Dispersion (ug/m3)	Downwash (ug/m3)
DAP			
Particulate Matter	1.1(1)	10	13
	1.9(2)	8	6
24-Hour SO_2	1.1(3)	10	15
	1.9(2)	8	6
3-Hour SO_2	1.1(4)	43	31
	1.9(2)	15	14
	2.5(5)	10	9
Third Product Load-Out			
Particulate Matter	1.1(1)	1.1	0.7
	1.9(2)	0.6	0.3

(1) Point of maximum impact for all particulate matter sources and for DAP plant emissions.

(2) Distance to nearest New Wales property line.

(3) Point of maximum 24-hour impact for emissions from DAP plant. Point of maximum 24-hour impact for all SO_2 sources is between 1.9 and 3.2 km.

(4) Point of maximum 3-hour impact for emissions from DAP plant. Point of maximum 3-hour impact for all sources is 2.5+ km.

(5) Point of maximum 3-hour impact for SO_2 emissions from all sources.

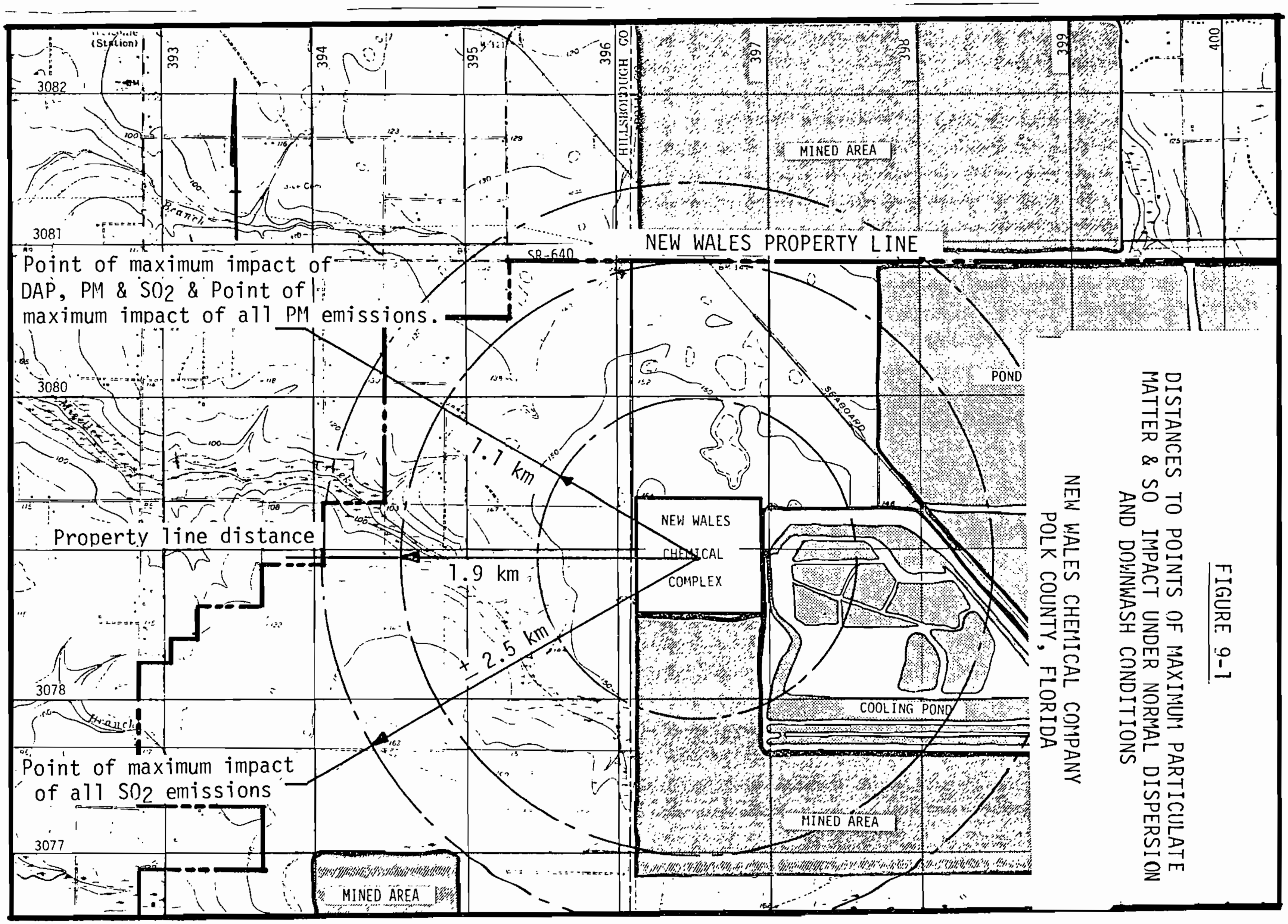


FIGURE 9-1

DISTANCES TO POINTS OF MAXIMUM PARTICULATE MATTER & SO IMPACT UNDER NORMAL DISPERSION AND DOWNWASH CONDITIONS

NEW WALES CHEMICAL COMPANY
POLK COUNTY, FLORIDA

REFERENCES
SECTION 9

1. Turner, D.B., Workbook of Atmospheric Dispersion Estimates, AP-26, US Department of HEW, Cincinnati, Ohio 1969.

ATTACHMENT 1

RUN NO.	IMPACT ANALYSIS
1	24-Hr PM Emissions from DAP - Normal Dispersion
2	24-Hr PM Emissions from DAP - Downwash
3	24-Hr SO_2 Emissions from DAP - Normal Dispersion
4	24-Hr SO_2 Emissions from DAP - Downwash
5	3-Hr SO_2 Emissions from DAP - Normal Dispersion
6	3-Hr SO_2 Emissions from DAP - Downwash
7	24-Hr PM Emissions from Third Product Load-Out - Normal Dispersion
8	24-Hr PM Emissions from Third Product Load-Out - Downwash

```
NEW WALES NORMAL DISPERSION ANALYSIS - DAP, NORMAL DISPERSION  24-HR PART MATTER  VERSION 78310
PINA =    0.02000 PINL =    0.02000
                    SOURCE        WIND  INCREASE
                   INCLUDED       WITH   HEIGHT

   POINT            YES                  NO

    AREA            NO                   NO

HORIZONTAL
LINE SOURCE         NO                   NO

   CURVE
PATH SOURCE         NO                   NO

  SPECIAL
LINE SOURCE         NO                   NO

  SPECIAL
PATH SOURCE         NO                   NO            AVERAGE      YES    DIURNAL     NO      HEIGHT AT WIND SPEED    10.0 METERS


* * * P O I N T    S O U R C E S * * *
      NO.      POINT     PHYSICAL       STACK        STACK      STACK      VOLUME        COORDINATES          INITIAL  SIGMAS
              SOURCE      HEIGHT        TEMP          GAS      DIAMETER     FLOW       EAST      NORTH          Y          Z
             STRENGTH    (METERS)     (DEG-K)     VELOCITY   (METERS)  (CU M/SEC)    (KM)       (KM)         (M)        (M)
              (G/SEC)                              (M/SEC)

       1         4.32       36.6        310.0       20.10        1.83       0.0      10.000     10.000         1.0        1.0
       2         2.54       24.4        310.0       10.10        1.87       0.0      10.000     10.000         1.0        1.0

 * * R E C E P T O R S * * *

      NO.     RREC(KM)   SREC(KM)      Z (M)

        1      10.500     10.000        0.0
        2      10.700     10.000        0.0
        3      10.900     10.000        0.0
        4      11.100     10.000        0.0
        5      11.300     10.000        0.0
        6      11.500     10.000        0.0
        7      11.700     10.000        0.0
        8      11.900     10.000        0.0
        9      12.100     10.000        0.0
       10      10.900      9.800        0.0
       11      10.900      9.900        0.0
       12      10.900     10.100        0.0
       13      10.900     10.200        0.0
       14      12.100      9.800        0.0
       15      12.100      9.900        0.0
       16      12.100     10.100        0.0
       17      12.100     10.200        0.0
       18      10.900     10.000       10.0
       19      10.900     10.000       20.0
       20      10.900     10.000       30.0
       21      10.900     10.000       40.0
       22      12.100     10.000       10.0
       23      12.100     10.000       20.0
       24      12.100     10.000       30.0
       25      12.100     10.000       40.0

 * * M E T E O R O L O G Y * * *

      NO.   THETA(DEG)      U (M/SEC)      KST     HL (M)    T (DEG-K)                DIURNAL  VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                                          HORIZONAL    CURVED     SPECIAL     SPECIAL
                                                                                    POINT       AREA        LINE        PATH        LINE        PATH
       1.        228.           3.6          4       881.       295.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       2.        227.           3.1          5       954.       296.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       3.        263.           3.5          4       879.       295.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       4.        267.           3.6          4       878.       296.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       5.        259.           4.1          4       878.       297.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       6.        263.           4.1          4       877.       298.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       7.        275.           4.1          4       876.       298.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       8.        260.           3.6          4       875.       300.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
       9.        291.           4.1          4       875.       300.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
      10.        266.           4.1          4       874.       303.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
      11.        323.           5.1          4       873.       302.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
      12.        278.           3.6          4       872.       304.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
      13.        287.           4.6          4       871.       305.                1.0000      1.0000      1.0000      1.0000      1.0000      1.0000
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          14.        250.        6.2        4        871.       305.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          15.        276.        5.7        4        870.       306.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          16.        280.        5.7        4        869.       306.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          17.        278.        5.7        4        868.       302.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          18.        294.        5.1        4        868.       300.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          19.        279.        4.1        4        867.       300.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          20.        281.        4.6        4        866.       300.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          21.        233.        4.1        4        865.       298.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          22.        273.        5.7        4        864.       298.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          23.        277.        3.6        4        864.       297.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
          24.        277.        3.6        4        876.       296.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000


AVERAGE CONCENTRATIONS FOR  24 HOURS.

 * * C O N C E N T R A T I O N S   A T   R E C E P T O R S * * *
     CONCENTRATIONS IN GRAMS PER CUBIC METER                       FROM        FROM       FROM       FROM
HOUR RECEPTOR      RECEPTOR COORDINATES      FROM          FROM    HORIZONAL   CURVED     SPECIAL    SPECIAL
        NO.      EAST      NORTH    HEIGHT   POINTS        AREAS   LINES       PATHS      LINES      PATHS       TOTAL

  0      1      10.500    10.000    0.0      7.904E-06 0.0         0.0         0.0        0.0        0.0         7.904E-06
  0      2      10.700    10.000    0.0      7.411E-06 0.0         0.0         0.0        0.0        0.0         7.411E-06
  0      3      10.900    10.000    0.0      9.536E-06 0.0         0.0         0.0        0.0        0.0         9.536E-06
  0      4      11.100    10.000    0.0      9.945E-06 0.0         0.0         0.0        0.0        0.0         9.945E-06
  0      5      11.300    10.000    0.0      9.555E-06 0.0         0.0         0.0        0.0        0.0         9.555E-06
  0      6      11.500    10.000    0.0      8.945E-06 0.0         0.0         0.0        0.0        0.0         8.945E-06
  0      7      11.700    10.000    0.0      8.268E-06 0.0         0.0         0.0        0.0        0.0         8.268E-06
  0      8      11.900    10.000    0.0      7.599E-06 0.0         0.0         0.0        0.0        0.0         7.599E-06
  0      9      12.100    10.000    0.0      6.970E-06 0.0         0.0         0.0        0.0        0.0         6.970E-06
  0     10      10.900     9.800    0.0      9.615E-06 0.0         0.0         0.0        0.0        0.0         9.615E-06
  0     11      10.900     9.900    0.0      1.291E-05 0.0         0.0         0.0        0.0        0.0         1.291E-05
  0     12      10.900    10.100    0.0      8.567E-06 0.0         0.0         0.0        0.0        0.0         8.567E-06
  0     13      10.900    10.200    0.0      3.256E-06 0.0         0.0         0.0        0.0        0.0         3.256E-06
  0     14      12.100     9.800    0.0      7.312E-06 0.0         0.0         0.0        0.0        0.0         7.312E-06
  0     15      12.100     9.900    0.0      6.358E-06 0.0         0.0         0.0        0.0        0.0         6.359E-06
  0     16      12.100    10.100    0.0      7.883E-06 0.0         0.0         0.0        0.0        0.0         7.883E-06
  0     17      12.100    10.200    0.0      7.270E-06 0.0         0.0         0.0        0.0        0.0         7.270E-06
  0     18      10.900    10.000   10.00     1.061E-05 0.0         0.0         0.0        0.0        0.0         1.061E-05
  0     19      10.900    10.000   20.00     1.357E-05 0.0         0.0         0.0        0.0        0.0         1.357E-05
  0     20      10.900    10.000   30.00     1.761E-05 0.0         0.0         0.0        0.0        0.0         1.761E-05
  0     21      10.900    10.000   40.00     2.156E-05 0.0         0.0         0.0        0.0        0.0         2.155E-05
  0     22      12.100    10.000   10.00     6.989E-06 0.0         0.0         0.0        0.0        0.0         6.989E-06
  0     23      12.100    10.000   20.00     7.035E-06 0.0         0.0         0.0        0.0        0.0         7.035E-06
  0     24      12.100    10.000   30.00     7.077E-06 0.0         0.0         0.0        0.0        0.0         7.077E-06
  0     25      12.100    10.000   40.00     7.071E-06 0.0         0.0         0.0        0.0        0.0         7.071E-06



TCP OUTPUT CHARGE: $  .36
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NEW WALES DOWNWASH ANALYSIS - DAP PART MATTER- DOWNWASH                                     VERSION 78310
PINA =    0.02000 PINL =    0.02000
                   SOURCE        WIND  INCREASE
                  INCLUDED       WITH   HEIGHT

    POINT          YES                  NO

     AREA          NO                   NO

HORIZONTAL
LINE SOURCE        NO                   NO

   CURVE
PATH SOURCE        NO                   NO

  SPECIAL
LINE SOURCE        NO                   NO

  SPECIAL
PATH SOURCE        NO                   NO          AVERAGE     YES   DIURNAL     NO     HEIGHT AT WIND SPEED   10.0 METERS


* * * P O I N T   S O U R C E S * * *
      NO.     POINT     PHYSICAL    STACK       STACK       STACK      VOLUME         COORDINATES         INITIAL SIGMAS
             SOURCE      HEIGHT     TEMP         GAS       DIAMETER     FLOW        EAST       NORTH         Y          Z
            STRENGTH   (METERS)   (DEG-K)     VELOCITY    (METERS)  (CU M/SEC)     (KM)       (KM)         (M)        (M)
             (G/SEC)                           (M/SEC)

      1         4.32      36.6     310.0        1.00        1.83        0.0     10.000     10.000        17.4       17.4
      2         0.54      24.4     310.0        1.00        1.83        0.0     10.000     10.000        11.6       11.6

 * * R E C E P T O R S * * *

      NO.     RREC(KM)   SREC(KM)     Z (M)

        1      10.500     10.000       0.0
        2      10.700     10.000       0.0
        3      10.900     10.000       0.0
        4      11.100     10.000       0.0
        5      11.300     10.000       0.0
        6      11.500     10.000       0.0
        7      11.700     10.000       0.0
        8      11.900     10.000       0.0
        9      12.100     10.000       0.0
       10      10.900      9.800       0.0
       11      10.900      9.900       0.0
       12      10.900     10.100       0.0
       13      10.900     10.200       0.0
       14      12.100      9.800       0.0
       15      12.100      9.900       0.0
       16      12.100     10.100       0.0
       17      12.100     10.200       0.0

 * * M E T E O R O L O G Y * * *

      NO.  THETA(DEG)     U (M/SEC)     KST    HL  (M)   T (DEG-K)           DIURNAL VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                                  HORIZONTAL   CURVED    SPECIAL    SPECIAL
                                                                             POINT       AREA       LINE        PATH      LINE       PATH
       1.       228.          3.6         3       881.       296.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       2.       227.          3.1         3       954.       296.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       3.       263.          3.6         3       879.       295.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       4.       267.          3.6         3       878.       296.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       5.       259.          4.1         3       878.       297.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       6.       263.          4.1         3       877.       298.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       7.       275.          4.1         3       876.       298.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       8.       269.          3.6         3       875.       300.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
       9.       291.          4.1         3       875.       300.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      10.       266.          4.1         3       874.       303.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      11.       323.          5.1         3       873.       302.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      12.       278.          3.6         3       872.       304.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      13.       287.          4.6         3       871.       305.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      14.       250.          6.2         3       871.       305.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      15.       276.          5.7         3       870.       306.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      16.       280.          5.7         3       869.       306.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      17.       278.          5.7         3       868.       302.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      18.       294.          5.1         3       868.       300.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      19.       279.          4.1         3       867.       300.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      20.       281.          4.6         3       866.       300.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      21.       233.          4.1         3       865.       298.            1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
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    22.      238.       5.7        3      864.      298.           1.0000  1.0000  1.0000  1.0000  1.0000  1.0000
    23.      270.       3.6        3      864.      297.           1.0000  1.0000  1.0000  1.0000  1.0000  1.0000
    24.      267.       3.6        3      876.      296.           1.0000  1.0000  1.0000  1.0000  1.0000  1.0000


AVERAGE CONCENTRATIONS FOR  24 HOURS.

 **C O N C E N T R A T I O N S   A T   R E C E P T O R S***
    CONCENTRATIONS IN GRAMS PER CUBIC METER                         FROM       FROM      FROM      FROM
HOUR RECEPTOR     RECEPTOR COORDINATES    FROM       FROM           HORIZONAL  CURVED    SPECIAL   SPECIAL
       NO.      EAST     NORTH   HEIGHT   POINTS     AREAS          LINES      PATHS     LINES     PATHS      TOTAL

   0     1     10.500   10.000   0.0      3.901E-05 0.0            0.0        0.0       0.0       0.0        3.901E-05
   0     2     10.700   10.000   0.0      2.580E-05 0.0            0.0        0.0       0.0       0.0        2.580E-05
   0     3     10.900   10.000   0.0      1.818E-05 0.0            0.0        0.0       0.0       0.0        1.818E-05
   0     4     11.100   10.000   0.0      1.346E-05 0.0            0.0        0.0       0.0       0.0        1.346E-05
   0     5     11.300   10.000   0.0      1.035E-05 0.0            0.0        0.0       0.0       0.0        1.035E-05
   0     6     11.500   10.000   0.0      8.204E-06 0.0            0.0        0.0       0.0       0.0        8.204E-06
   0     7     11.700   10.000   0.0      6.662E-06 0.0            0.0        0.0       0.0       0.0        6.662E-06
   0     8     11.900   10.000   0.0      5.517E-06 0.0            0.0        0.0       0.0       0.0        5.517E-06
   0     9     12.100   10.000   0.0      4.645E-06 0.0            0.0        0.0       0.0       0.0        4.645E-06
   0    10     10.900    9.800   0.0      1.230E-05 0.0            0.0        0.0       0.0       0.0        1.230E-05
   0    11     10.900    9.900   0.0      1.662E-05 0.0            0.0        0.0       0.0       0.0        1.662E-05
   0    12     10.900   10.100   0.0      1.512E-05 0.0            0.0        0.0       0.0       0.0        1.512E-05
   0    13     10.900   10.200   0.0      8.426E-06 0.0            0.0        0.0       0.0       0.0        8.426E-06
   0    14     12.100    9.800   0.0      4.300E-06 0.0            0.0        0.0       0.0       0.0        4.300E-06
   0    15     12.100    9.900   0.0      4.524E-06 0.0            0.0        0.0       0.0       0.0        4.524E-06
   0    16     12.100   10.100   0.0      4.567E-06 0.0            0.0        0.0       0.0       0.0        4.567E-06
   0    17     12.100   10.200   0.0      4.156E-06 0.0            0.0        0.0       0.0       0.0        4.156E-06



TCP OUTPUT CHARGE: $  .28
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NEW WALES NORMAL DISPERSION ANALYSIS - DAP SO2, NORMAL DISPERSION  24-HR SO2        VERSION 78310
PINA =    0.02000 PINL =    0.02000
                  SOURCE        WIND  INCREASE
                  INCLUDED      WITH  HEIGHT

   POINT            YES              NO

   AREA             NO               NO

HORIZONTAL
LINE SOURCE         NO               NO

    CURVE
PATH SOURCE         NO               NO

  SPECIAL
LINE SOURCE         NO               NO

  SPECIAL
PATH SOURCE         NO               NO             AVERAGE      YES   DIURNAL     NO     HEIGHT AT WIND SPEED   10.0 METERS


* * * P O I N T   S O U R C E S * * *
     NO.     POINT     PHYSICAL    STACK       STACK      STACK     VOLUME       COORDINATES         INITIAL SIGMAS
             SOURCE     HEIGHT     TEMP         GAS      DIAMETER    FLOW       EAST      NORTH         Y          Z
            STRENGTH   (METERS)   (DEG-K)    VELOCITY   (METERS)  (CU M/SEC)    (KM)      (KM)         (M)        (M)
             (G/SEC)                          (M/SEC)

     1         5.50       76.6      310.0       20.10       1.83       0.0     10.000    10.000         1.0        1.0

  * * R E C E P T O R S * * *

     NO.     RREC(KM)   SREC(KM)     Z (M)

       1      10.500     10.000       0.0
       2      10.700     10.000       0.0
       3      10.900     10.000       0.0
       4      11.100     10.000       0.0
       5      11.300     10.000       0.0
       6      11.500     10.000       0.0
       7      11.700     10.000       0.0
       8      11.900     10.000       0.0
       9      12.100     10.000       0.0
      10      10.900      9.800       0.0
      11      10.900      9.900       0.0
      12      10.900     10.100       0.0
      13      10.900     10.200       0.0
      14      12.100      9.800       0.0
      15      12.100      9.900       0.0
      16      12.100     10.100       0.0
      17      12.100     10.200       0.0
      18      10.900     10.000      10.0
      19      10.900     10.000      20.0
      20      10.900     10.000      30.0
      21      10.900     10.000      40.0
      22      12.100     10.000      10.0
      23      12.100     10.000      20.0
      24      12.100     10.000      30.0
      25      12.100     10.000      40.0

  * * M E T E O R O L O G Y * * *

     NO.  THETA(DEG)     U (M/SEC)     KST    HL (M)   T (DEG-K)           DIURNAL VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                                HORIZONAL  CURVED    SPECIAL   SPECIAL
                                                                          POINT      AREA       LINE      PATH      LINE      PATH
      1.        229.         3.6          4      931.      296.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      2.        227.         3.1          5      954.      295.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      3.        263.         3.6          4      879.      295.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      4.        267.         3.6          4      878.      296.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      5.        259.         4.1          4      878.      297.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      6.        263.         4.1          4      877.      295.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      7.        275.         4.1          4      876.      298.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      8.        269.         3.6          4      875.      300.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      9.        291.         4.1          4      875.      300.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
     10.        266.         4.1          4      874.      303.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
     11.        323.         5.1          4      873.      302.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
     12.        278.         3.6          4      872.      304.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
     13.        237.         4.6          4      871.      305.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
     14.        259.         6.2          4      871.      305.          1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
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    15.        276.        5.7         4        870.      306.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    16.        290.        5.7         4        869.      305.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    17.        279.        5.7         4        868.      302.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    18.        294.        5.1         4        868.      300.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    19.        279.        4.1         4        867.      300.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    20.        281.        4.6         4        866.      300.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    21.        233.        4.1         4        865.      298.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    22.        239.        5.7         4        864.      298.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    23.        270.        3.6         4        864.      297.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
    24.        267.        3.6         4        876.      296.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000



AVERAGE CONCENTRATIONS FOR  24 HOURS.

 * * C O N C E N T R A T I O N S   A T   R E C E P T O R S * * *

,    CONCENTRATIONS IN GRAMS PER CUBIC METER                      FROM        FROM      FROM       FROM
HOUR RECEPTOR    RECEPTOR COORDINATES      FROM         FROM      HORIZONAL   CURVED   SPECIAL    SPECIAL
       NO.       EAST     NORTH   HEIGHT   POINTS       AREAS     LINES       PATHS     LINES      PATHS       TOTAL

  0     1     10.500    10.000    0.0     1.996E-06  0.0        0.0         0.0       0.0        0.0        1.996E-06
  0     2     10.700    10.000    0.0     5.882E-06  0.0        0.0         0.0       0.0        0.0        5.882E-06
  0     3     10.900    10.000    0.0     8.843E-06  0.0        0.0         0.0       0.0        0.0        8.843E-06
  0     4     11.100    10.000    0.0     9.827E-06  0.0        0.0         0.0       0.0        0.0        9.827E-06
  0     5     11.300    10.000    0.0     9.752E-06  0.0        0.0         0.0       0.0        0.0        9.752E-06
  0     6     11.500    10.000    0.0     9.322E-06  0.0        0.0         0.0       0.0        0.0        9.322E-06
  0     7     11.700    10.000    0.0     8.741E-06  0.0        0.0         0.0       0.0        0.0        8.741E-06
  0     8     11.900    10.000    0.0     8.118E-06  0.0        0.0         0.0       0.0        0.0        8.118E-06
  0     9     12.100    10.000    0.0     7.505E-06  0.0        0.0         0.0       0.0        0.0        7.505E-06
  0    10     10.900     9.800    0.0     9.644E-06  0.0        0.0         0.0       0.0        0.0        9.644E-06
  0    11     10.900     9.900    0.0     1.276E-05  0.0        0.0         0.0       0.0        0.0        1.276E-05
  0    12     10.900    10.100    0.0     7.838E-06  0.0        0.0         0.0       0.0        0.0        7.838E-06
  0    13     10.900    10.200    0.0     3.033E-06  0.0        0.0         0.0       0.0        0.0        3.033E-06
  0    14     12.100     9.800    0.0     7.973E-06  0.0        0.0         0.0       0.0        0.0        7.973E-06
  0    15     12.100     9.900    0.0     6.887E-06  0.0        0.0         0.0       0.0        0.0        6.887E-06
  0    16     12.100    10.100    0.0     8.474E-06  0.0        0.0         0.0       0.0        0.0        8.474E-06
  0    17     12.100    10.200    0.0     7.815E-06  0.0        0.0         0.0       0.0        0.0        7.815E-06
  0    18     10.900    10.000   10.00    1.012E-05  0.0        0.0         0.0       0.0        0.0        1.012E-05
  0    19     10.900    10.000   20.00    1.367E-05  0.0        0.0         0.0       0.0        0.0        1.367E-05
  0    20     10.900    10.000   30.00    1.864E-05  0.0        0.0         0.0       0.0        0.0        1.864E-05
  0    21     10.900    10.000   40.00    2.372E-05  0.0        0.0         0.0       0.0        0.0        2.372E-05
  0    22     12.100    10.000   10.00    7.542E-06  0.0        0.0         0.0       0.0        0.0        7.542E-06
  0    23     12.100    10.000   20.00    7.636E-06  0.0        0.0         0.0       0.0        0.0        7.636E-06
  0    24     12.100    10.000   30.00    7.748E-06  0.0        0.0         0.0       0.0        0.0        7.748E-06
  0    25     12.100    10.000   40.00    7.822E-06  0.0        0.0         0.0       0.0        0.0        7.822E-06



TCP OUTPUT CHARGE: $  .36
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NEW WALES DOWNWASH ANALYSIS -|DAP 24-HR SO2- DOWNWASH |                                    VERSION 78310
PINA =    0.02000 PINL =    0.02000
                 SOURCE      WIND  INCREASE
                INCLUDED     WITH   HEIGHT
   POINT          YES                NO

   AREA           NO                 NO

HORIZONTAL
LINE SOURCE       NO                 NO

   CURVE
PATH SOURCE       NO                 NO

  SPECIAL
LINE SOURCE       NO                 NO

  SPECIAL
PATH SOURCE       NO                 NO           AVERAGE     YES   DIURNAL    NO     HEIGHT AT WIND SPEED    10.0 METERS


* * * P O I N T   S O U R C E S * * *
     NO.     POINT      PHYSICAL     STACK        STACK       STACK      VOLUME           COORDINATES            INITIAL SIGMAS
            SOURCE       HEIGHT      TEMP          GAS       DIAMETER     FLOW          EAST        NORTH          Y              Z
           STRENGTH     (METERS)    (DEG-K)     VELOCITY    (METERS)   (CU M/SEC)       (KM)         (KM)          (M)            (M)
           (G/SEC)                               (M/SEC)

      1        5.50        36.6       310.0        1.00        1.83        0.C        10.000       10.000        17.4           17.4

  * * R E C E P T O R S * * *

     NO.     RREC(KM)   SREC(KM)     Z (M)

       1      10.500     10.000       0.0
       2      10.700     10.000       0.0
       3      10.900     10.000       0.C
       4      11.100     10.000       0.C
       5      11.300     10.000       0.0
       6      11.500     10.000       0.0
       7      11.700     10.000       0.0
       8      11.900     10.000       0.0
       9      12.100     10.000       0.0
      10      10.900      9.800       0.0
      11      10.900      9.900       0.0
      12      10.900     10.100       0.0
      13      10.900     10.200       0.0
      14      12.100      9.800       0.0
      15      12.100      9.900       0.0
      16      12.100     10.100       0.0
      17      12.100     10.200       0.0

  * * M E T E O R O L O G Y * * *

     NO.   THETA(DEG)     U (M/SEC)      KST     HL (M)    T (DEG-K)         DIURNAL VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                                HORIZONAL    CURVED     SPECIAL     SPECIAL
                                                                              POINT      AREA       LINE        PATH        LINE        PATH
      1.      228.          3.6            3       881.       296.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      2.      227.          3.1            3       954.       296.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      3.      263.          3.6            3       879.       295.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      4.      267.          3.6            3       878.       296.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      5.      259.          4.1            3       878.       297.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      6.      263.          4.1            3       877.       298.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      7.      275.          4.1            3       876.       299.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      8.      269.          3.6            3       875.       300.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
      9.      291.          4.1            3       875.       300.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     10.      266.          4.1            3       874.       303.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     11.      323.          5.1            3       873.       302.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     12.      278.          3.6            3       872.       304.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     13.      287.          4.6            3       871.       305.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     14.      250.          6.2            3       871.       305.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     15.      276.          5.7            3       870.       306.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     16.      280.          5.7            3       869.       306.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     17.      278.          5.7            3       868.       302.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     18.      294.          5.1            3       868.       300.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     19.      279.          4.1            3       867.       300.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     20.      281.          4.6            3       866.       300.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     21.      233.          4.1            3       865.       298.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
     22.      238.          5.7            3       864.       298.          1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
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        23.      270.       3.6        3     864.      297.              1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
        24.      267.       3.6        3     876.      296.              1.0000   1.0000   1.0000   1.0000   1.0000   1.0000


AVERAGE CONCENTRATIONS FOR  24 HOURS.

 **C O N C E N T R A T I O N S   A T   R E C E P T O R S***
    CONCENTRATIONS IN GRAMS PER CUBIC METER                      FROM       FROM      FROM      FROM
HOUR RECEPTOR    RECEPTOR COORDINATES     FROM        FROM       HORIZONAL  CURVED   SPECIAL   SPECIAL
       NO.       EAST     NORTH   HEIGHT   POINTS      AREAS      LINES      PATHS     LINES     PATHS       TOTAL

  0     1       10.500   10.000   0.0      4.262E-05 0.0         0.0        0.0       0.0       0.0        4.262E-05
  0     2       10.700   10.000   0.0      2.848E-05 0.0         0.0        0.0       0.0       0.0        2.848E-05
  0     3       10.900   10.000   0.0      2.019E-05 0.0         0.0        0.0       0.0       0.0        2.019E-05
  0     4       11.100   10.000   0.0      1.500E-05 0.0         0.0        0.0       0.0       0.0        1.500E-05
  0     5       11.300   10.000   0.0      1.157E-05 0.0         0.0        0.0       0.0       0.0        1.157E-05
  0     6       11.500   10.000   0.0      9.189E-06 0.0         0.0        0.0       0.0       0.0        9.189E-06
  0     7       11.700   10.000   0.0      7.472E-06 0.0         0.0        0.0       0.0       0.0        7.472E-06
  0     8       11.900   10.000   0.0      6.196E-06 0.0         0.0        0.0       0.0       0.0        6.196E-06
  0     9       12.100   10.000   0.0      5.221E-06 0.0         0.0        0.0       0.0       0.0        5.221E-06
  0    10       10.900    9.800   0.0      1.369E-05 0.0         0.0        0.0       0.0       0.0        1.369E-05
  0    11       10.900    9.900   0.0      1.847E-05 0.0         0.0        0.0       0.0       0.0        1.847E-05
  0    12       10.900   10.100   0.0      1.678E-05 0.0         0.0        0.0       0.0       0.0        1.678E-05
  0    13       10.900   10.200   0.0      9.393E-06 0.0         0.0        0.0       0.0       0.0        9.393E-06
  0    14       12.100    9.800   0.0      4.834E-06 0.0         0.0        0.0       0.0       0.0        4.834E-06
  0    15       12.100    9.900   0.0      5.096E-06 0.0         0.0        0.0       0.0       0.0        5.086E-06
  0    16       12.100   10.100   0.0      5.131E-06 0.0         0.0        0.0       0.0       0.0        5.131E-06
  0    17       12.100   10.200   0.0      4.668E-06 0.0         0.0        0.0       0.0       0.0        4.668E-06



TCP OUTPUT CHARGE: $  .28
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NEW WALES DOWNWASH ANALYSIS - DAP 3-HR SO2 - NORMAL DISPERSION                          VERSION 78310
PINA =    0.02000 PINL =    0.02000
                 SOURCE     WIND INCREASE
                 INCLUDED   WITH  HEIGHT
    POINT          YES             NO

    AREA           NO              NO

HORIZONTAL
LINE SOURCE        NO              NO

   CURVE
PATH SOURCE        NO              NO

  SPECIAL
LINE SOURCE        NO              NO

  SPECIAL
PATH SOURCE        NO              NO         AVERAGE    YES   DIURNAL    NO     HEIGHT AT WIND SPEED   10.0 METERS


* * * P O I N T   S O U R C E S * * *
     NO.    POINT    PHYSICAL    STACK       STACK      STACK     VOLUME        COORDINATES        INITIAL SIGMAS
            SOURCE    HEIGHT     TEMP         GAS     DIAMETER     FLOW       EAST      NORTH        Y          Z
           STRENGTH  (METERS)   (DEG-K)    VELOCITY   (METERS)  (CU M/SEC)    (KM)       (KM)       (M)        (M)
           (G/SEC)                          (M/SEC)

      1       5.50      36.6     310.0       20.10       1.83       0.0      10.000     10.000      1.0        1.0

 * * R E C E P T O R S * * *

     NO.     RREC(KM)  SREC(KM)     Z (M)

       1     10.500    10.000       0.0
       2     10.700    10.000       0.0
       3     10.900    10.000       0.0
       4     11.100    10.000       0.0
       5     11.300    10.000       0.0
       6     11.500    10.000       0.0
       7     11.700    10.000       0.0
       8     11.900    10.000       0.0
       9     12.100    10.000       0.0
      10     12.300    10.000       0.0
      11     12.500    10.000       0.0
      12     12.700    10.000       0.0
      13     12.900    10.000       0.0
      14     13.100    10.000       0.0
      15     10.900     9.800       0.0
      16     10.900     9.900       0.0
      17     10.900    10.100       0.0
      18     10.900    10.200       0.0
      19     12.100     9.800       0.0
      20     12.100     9.900       0.0
      21     12.100    10.100       0.0
      22     12.100    10.200       0.0

 * * M E T E O R O L O G Y * * *

     NO.  THETA(DEG)     U (M/SEC)     KST    HL (M)   T (DEG-K)          DIURNAL VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                            HORIZONTAL   CURVED    SPECIAL    SPECIAL
                                                                          POINT      AREA      LINE       PATH       LINE       PATH
      1.        272.          4.6          4     1413.       301.         1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      2.        268.          4.6          4     1412.       301.         1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      3.        271.          5.1          4     1411.       302.         1.0000    1.0000    1.0000    1.0000    1.0000    1.0000

 * * C O N C E N T R A T I O N S   A T   R E C E P T O R S * * *

    CONCENTRATIONS IN GRAMS PER CUBIC METER                       FROM        FROM      FROM      FROM
HOUR RECEPTOR      RECEPTOR COORDINATES      FROM          FROM   HORIZONTAL  CURVED    SPECIAL   SPECIAL
        NO.       EAST      NORTH    HEIGHT   POINTS        AREAS  LINES       PATHS     LINES     PATHS        TOTAL


  1     1       10.500    10.000    0.0      1.120E-05 0.0     0.0         0.0       0.0       0.0          1.120E-05
  1     2       10.700    10.000    0.0      2.986E-05 0.0     0.0         0.0       0.0       0.0          2.986E-05
  1     3       10.900    10.000    0.0      4.030E-05 0.0     0.0         0.0       0.0       0.0          4.030E-05
  1     4       11.100    10.000    0.0      4.197E-05 0.0     0.0         0.0       0.0       0.0          4.197E-05
  1     5       11.300    10.000    0.0      4.008E-05 0.0     0.0         0.0       0.0       0.0          4.008E-05
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   1    6     11.500    10.000    0.0        3.728E-05 0.0        0.0        0.0        0.0        0.0        3.728E-05
   1    7     11.700    10.000    0.0        3.426E-05 0.0        0.0        0.0        0.0        0.0        3.426E-05
   1    8     11.900    10.000    0.0        3.135E-05 0.0        0.0        0.0        0.0        0.0        3.135E-05
   1    9     12.100    10.000    0.0        2.866E-05 0.0        0.0        0.0        0.0        0.0        2.866E-05
   1   10     12.300    10.000    0.0        2.623E-05 0.0        0.0        0.0        0.0        0.0        2.623E-05
   1   11     12.500    10.000    0.0        2.406E-05 0.0        0.0        0.0        0.0        0.0        2.406E-05
   1   12     12.700    10.000    0.0        2.212E-05 0.0        0.0        0.0        0.0        0.0        2.212E-05
   1   13     12.900    10.000    0.0        2.040E-05 0.0        0.0        0.0        0.0        0.0        2.040E-05
   1   14     13.100    10.000    0.0        1.888E-05 0.0        0.0        0.0        0.0        0.0        1.888E-05
   1   15     10.900     9.800    0.0        1.281E-06 0.0        0.0        0.0        0.0        0.0        1.281E-06
   1   16     10.900     9.900    0.0        2.524E-05 0.0        0.0        0.0        0.0        0.0        2.524E-05
   1   17     10.900    10.100    0.0        4.941E-06 0.0        0.0        0.0        0.0        0.0        4.941E-06
   1   18     10.900    10.200    0.0        4.405E-08 0.0        0.0        0.0        0.0        0.0        4.405E-08
   1   19     12.100     9.800    0.0        2.132E-05 0.0        0.0        0.0        0.0        0.0        2.132E-05
   1   20     12.100     9.900    0.0        3.257E-05 0.0        0.0        0.0        0.0        0.0        3.257E-05
   1   21     12.100    10.100    0.0        1.446E-05 0.0        0.0        0.0        0.0        0.0        1.446E-05
   1   22     12.100    10.200    0.0        4.161E-06 0.0        0.0        0.0        0.0        0.0        4.161E-06

 * * C O N C E N T R A T I O N S   A T    R E C E P T O R S * * *

,    CONCENTRATIONS IN GRAMS PER CUBIC METER                     FROM       FROM       FROM       FROM
HOUR RECEPTOR     RECEPTOR COORDINATES     FROM        FROM      HORIZONAL  CURVED     SPECIAL    SPECIAL
        NO.      EAST      NORTH    HEIGHT    POINTS      AREAS     LINES      PATHS      LINES      PATHS        TOTAL


   2    1     10.500    10.000    0.0        1.120E-05 0.0        0.0        0.0        0.0        0.0        1.120E-05
   2    2     10.700    10.000    0.0        2.985E-05 0.0        0.0        0.0        0.0        0.0        2.985E-05
   2    3     10.900    10.000    0.0        4.030E-05 0.0        0.0        0.0        0.0        0.0        4.030E-05
   2    4     11.100    10.000    0.0        4.197E-05 0.0        0.0        0.0        0.0        0.0        4.197E-05
   2    5     11.300    10.000    0.0        4.008E-05 0.0        0.0        0.0        0.0        0.0        4.008E-05
   2    6     11.500    10.000    0.0        3.727E-05 0.0        0.0        0.0        0.0        0.0        3.727E-05
   2    7     11.700    10.000    0.0        3.426E-05 0.0        0.0        0.0        0.0        0.0        3.426E-05
   2    8     11.900    10.000    0.0        3.135E-05 0.0        0.0        0.0        0.0        0.0        3.135E-05
   2    9     12.100    10.000    0.0        2.866E-05 0.0        0.0        0.0        0.0        0.0        2.866E-05
   2   10     12.300    10.000    0.0        2.623E-05 0.0        0.0        0.0        0.0        0.0        2.623E-05
   2   11     12.500    10.000    0.0        2.406E-05 0.0        0.0        0.0        0.0        0.0        2.406E-05
   2   12     12.700    10.000    0.0        2.212E-05 0.0        0.0        0.0        0.0        0.0        2.212E-05
   2   13     12.900    10.000    0.0        2.040E-05 0.0        0.0        0.0        0.0        0.0        2.040E-05
   2   14     13.100    10.000    0.0        1.888E-05 0.0        0.0        0.0        0.0        0.0        1.888E-05
   2   15     10.900     9.800    0.0        4.404E-08 0.0        0.0        0.0        0.0        0.0        4.404E-08
   2   16     10.900     9.900    0.0        4.940E-06 0.0        0.0        0.0        0.0        0.0        4.940E-06
   2   17     10.900    10.100    0.0        2.524E-05 0.0        0.0        0.0        0.0        0.0        2.524E-05
   2   18     10.900    10.200    0.0        1.281E-06 0.0        0.0        0.0        0.0        0.0        1.281E-06
   2   19     12.100     9.800    0.0        4.160E-06 0.0        0.0        0.0        0.0        0.0        4.160E-06
   2   20     12.100     9.900    0.0        1.446E-05 0.0        0.0        0.0        0.0        0.0        1.446E-05
   2   21     12.100    10.100    0.0        3.257E-05 0.0        0.0        0.0        0.0        0.0        3.257E-05
   2   22     12.100    10.200    0.0        2.132E-05 0.0        0.0        0.0        0.0        0.0        2.132E-05

 * * C O N C E N T R A T I O N S   A T    R E C E P T O R S * * *

     CONCENTRATIONS IN GRAMS PER CUBIC METER                     FROM       FROM       FROM       FROM
HOUR RECEPTOR     RECEPTOR COORDINATES     FROM        FROM      HORIZONAL  CURVED     SPECIAL    SPECIAL
        NO.      EAST      NORTH    HEIGHT    POINTS      AREAS     LINES      PATHS      LINES      PATHS        TOTAL


   3    1     10.500    10.000    0.0        1.601E-05 0.0        0.0        0.0        0.0        0.0        1.601E-05
   3    2     10.700    10.000    0.0        3.677E-05 0.0        0.0        0.0        0.0        0.0        3.677E-05
   3    3     10.900    10.000    0.0        4.634E-05 0.0        0.0        0.0        0.0        0.0        4.634E-05
   3    4     11.100    10.000    0.0        4.670E-05 0.0        0.0        0.0        0.0        0.0        4.670E-05
   3    5     11.300    10.000    0.0        4.379E-05 0.0        0.0        0.0        0.0        0.0        4.379E-05
   3    6     11.500    10.000    0.0        4.023E-05 0.0        0.0        0.0        0.0        0.0        4.023E-05
   3    7     11.700    10.000    0.0        3.666E-05 0.0        0.0        0.0        0.0        0.0        3.666E-05
   3    8     11.900    10.000    0.0        3.334E-05 0.0        0.0        0.0        0.0        0.0        3.334E-05
   3    9     12.100    10.000    0.0        3.034E-05 0.0        0.0        0.0        0.0        0.0        3.034E-05
   3   10     12.300    10.000    0.0        2.768E-05 0.0        0.0        0.0        0.0        0.0        2.768E-05
   3   11     12.500    10.000    0.0        2.532E-05 0.0        0.0        0.0        0.0        0.0        2.532E-05
   3   12     12.700    10.000    0.0        2.324E-05 0.0        0.0        0.0        0.0        0.0        2.324E-05
   3   13     12.900    10.000    0.0        2.140E-05 0.0        0.0        0.0        0.0        0.0        2.140E-05
   3   14     13.100    10.000    0.0        1.978E-05 0.0        0.0        0.0        0.0        0.0        1.978E-05
   3   15     10.900     9.800    0.0        6.439E-07 0.0        0.0        0.0        0.0        0.0        6.439E-07
   3   16     10.900     9.900    0.0        1.937E-05 0.0        0.0        0.0        0.0        0.0        1.937E-05
   3   17     10.900    10.100    0.0        8.586E-06 0.0        0.0        0.0        0.0        0.0        8.586E-06
   3   18     10.900    10.200    0.0        1.199E-07 0.0        0.0        0.0        0.0        0.0        1.199E-07
   3   19     12.100     9.800    0.0        1.505E-05 0.0        0.0        0.0        0.0        0.0        1.505E-05
   3   20     12.100     9.900    0.0        2.816E-05 0.0        0.0        0.0        0.0        0.0        2.816E-05
   3   21     12.100    10.100    0.0        1.878E-05 0.0        0.0        0.0        0.0        0.0        1.878E-05
   3   22     12.100    10.200    0.0        6.655E-06 0.0        0.0        0.0        0.0        0.0        6.655E-06
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AVERAGE CONCENTRATIONS FOR   3 HOURS.

  **C O N C E N T R A T I O N S   A T   R E C E P T O R S***

     CONCENTRATIONS IN GRAMS PER CUBIC METER                          FROM      FROM      FROM      FROM
HOUR RECEPTOR     RECEPTOR COORDINATES     FROM        FROM      HORIZONAL CURVED   SPECIAL   SPECIAL
        NO.      EAST     NORTH   HEIGHT   POINTS      AREAS     LINES     PATHS     LINES     PATHS      TOTAL


  0      1      10.500   10.000   0.0      1.280E-05  0.0       0.0       0.0       0.0       0.0        1.280E-05
  0      2      10.700   10.000   0.0      3.216E-05  0.0       0.0       0.0       0.0       0.0        3.216E-05
  0      3      10.900   10.000   0.0      4.231E-05  0.0       0.0       0.0       0.0       0.0        4.231E-05
  0      4      11.100   10.000   0.0      4.354E-05  0.0       0.0       0.0       0.0       0.0        4.354E-05
  0      5      11.300   10.000   0.0      4.132E-05  0.0       0.0       0.0       0.0       0.0        4.132E-05
  0      6      11.500   10.000   0.0      3.826E-05  0.0       0.0       0.0       0.0       0.0        3.826E-05
  0      7      11.700   10.000   0.0      3.506E-05  0.0       0.0       0.0       0.0       0.0        3.506E-05
  0      8      11.900   10.000   0.0      3.201E-05  0.0       0.0       0.0       0.0       0.0        3.201E-05
  0      9      12.100   10.000   0.0      2.922E-05  0.0       0.0       0.0       0.0       0.0        2.922E-05
  0     10      12.300   10.000   0.0      2.671E-05  0.0       0.0       0.0       0.0       0.0        2.671E-05
  0     11      12.500   10.000   0.0      2.448E-05  0.0       0.0       0.0       0.0       0.0        2.448E-05
  0     12      12.700   10.000   0.0      2.249E-05  0.0       0.0       0.0       0.0       0.0        2.249E-05
  0     13      12.900   10.000   0.0      2.073E-05  0.0       0.0       0.0       0.0       0.0        2.073E-05
  0     14      13.100   10.000   0.0      1.918E-05  0.0       0.0       0.0       0.0       0.0        1.918E-05
  0     15      10.900    9.800   0.0      6.562E-07  0.0       0.0       0.0       0.0       0.0        6.562E-07
  0     16      10.900    9.900   0.0      1.652E-05  0.0       0.0       0.0       0.0       0.0        1.652E-05
  0     17      10.900   10.100   0.0      1.292E-05  0.0       0.0       0.0       0.0       0.0        1.292E-05
  0     18      10.900   10.200   0.0      4.816E-07  0.0       0.0       0.0       0.0       0.0        4.816E-07
  0     19      12.100    9.800   0.0      1.351E-05  0.0       0.0       0.0       0.0       0.0        1.351E-05
  0     20      12.100    9.900   0.0      2.506E-05  0.0       0.0       0.0       0.0       0.0        2.506E-05
  0     21      12.100   10.100   0.0      2.193E-05  0.0       0.0       0.0       0.0       0.0        2.193E-05
  0     22      12.100   10.200   0.0      1.071E-05  0.0       0.0       0.0       0.0       0.0        1.071E-05



TCP OUTPUT CHARGE: $  .08
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NEW WALES DOWNWASH ANALYSIS - CAP 3-HR SO2 - DOWNWASH                                   VERSION 78310
PINA =    0.02000 PINL =    0.02000
                 SOURCE       WIND INCREASE
                INCLUDED      WITH  HEIGHT
   POINT          YES                NO

   AREA           NO                 NO

HORIZONTAL
LINE SOURCE       NO                 NO

   CURVE
PATH SOURCE       NO                 NO

  SPECIAL
LINE SOURCE       NO                 NO

  SPECIAL
PATH SOURCE       NO                 NO          AVERAGE     YES   DIURNAL     NO      HEIGHT AT WIND SPEED   10.0 METERS


* * * P O I N T   S O U R C E S * * *
        NO.    POINT     PHYSICAL    STACK       STACK      STACK     VOLUME        COORDINATES          INITIAL SIGMAS
              SOURCE      HEIGHT      TEMP        GAS      DIAMETER    FLOW       EAST       NORTH          Y            Z
             STRENGTH    (METERS)   (DEG-K)    VELOCITY   (METERS)  (CU M/SEC)   (KM)        (KM)          (M)          (M)
              (G/SEC)                           (M/SEC)

         1       5.50       36.6      310.0       1.00        1.83       0.0     10.000     10.000         17.4         17.4

 * * R E C E P T O R S * * *

        NO.     RREC(KM)   SREC(KM)      Z (M)

          1     10.500     10.000        0.0
          2     10.700     10.000        0.0
          3     10.900     10.000        0.0
          4     11.100     10.000        0.0
          5     11.300     10.000        0.0
          6     11.500     10.000        0.0
          7     11.700     10.000        0.0
          8     11.900     10.000        0.0
          9     12.100     10.000        0.0
         10     12.300     10.000        0.0
         11     12.500     10.000        0.0
         12     12.700     10.000        0.0
         13     12.900     10.000        0.0
         14     13.100     10.000        0.0
         15     10.900      9.800        0.0
         16     10.900      9.900        0.0
         17     10.900     10.100        0.0
         18     10.900     10.200        0.0
         19     12.100      9.800        0.0
         20     12.100      9.900        0.0
         21     12.100     10.100        0.0
         22     12.100     10.200        0.0

 * * M E T E O R O L O G Y * * *

        NO.   THETA(DEG)     U (M/SEC)     KST    HL (M)   T (DEG-K)          DIURNAL VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                                HORIZONTAL   CURVED     SPECIAL    SPECIAL
                                                                             POINT       AREA      LINE       PATH       LINE       PATH
         1.       272.         4.6          3      1413.       301.         1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
         2.       268.         4.6          3      1412.       301.         1.0000     1.0000     1.0000     1.0000     1.0000     1.0000
         3.       271.         5.1          3      1411.       302.         1.0000     1.0000     1.0000     1.0000     1.0000     1.0000

 * * C O N C E N T R A T I O N S   A T   R E C E P T O R S * * *

   CONCENTRATIONS IN GRAMS PER CUBIC METER                         FROM        FROM       FROM       FROM
HOUR RECEPTOR    RECEPTOR COORDINATES      FROM         FROM      HORIZONTAL  CURVED     SPECIAL    SPECIAL
       NO.      EAST      NORTH    HEIGHT    POINTS        AREAS      LINES      PATHS      LINES      PATHS        TOTAL


  1      1     10.500    10.000    0.0       8.168E-05 0.0        0.0        0.0        0.0        0.0          8.168E-05
  1      2     10.700    10.000    0.0       5.734E-05 0.0        0.0        0.0        0.0        0.0          5.734E-05
  1      3     10.900    10.000    0.0       4.205E-05 0.0        0.0        0.0        0.0        0.0          4.205E-05
  1      4     11.100    10.000    0.0       3.206E-05 0.0        0.0        0.0        0.0        0.0          3.206E-05
  1      5     11.300    10.000    0.0       2.523E-05 0.0        0.0        0.0        0.0        0.0          2.523E-05
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   1    6     11.500   10.000   0.0      2.038E-05 0.0      0.0      0.0      0.0      0.0      2.038E-05
   1    7     11.700   10.000   0.0      1.681E-05 0.0      0.0      0.0      0.0      0.0      1.681E-05
   1    8     11.900   10.000   0.0      1.411E-05 0.0      0.0      0.0      0.0      0.0      1.411E-05
   1    9     12.100   10.000   0.0      1.202E-05 0.0      0.0      0.0      0.0      0.0      1.202E-05
   1   10     12.300   10.000   0.0      1.037E-05 0.0      0.0      0.0      0.0      0.0      1.037E-05
   1   11     12.500   10.000   0.0      9.042E-06 0.0      0.0      0.0      0.0      0.0      9.042E-06
   1   12     12.700   10.000   0.0      7.958E-06 0.0      0.0      0.0      0.0      0.0      7.958E-06
   1   13     12.900   10.000   0.0      7.062E-06 0.0      0.0      0.0      0.0      0.0      7.062E-06
   1   14     13.100   10.000   0.0      6.312E-06 0.0      0.0      0.0      0.0      0.0      6.312E-06
   1   15     10.900    9.800   0.0      1.281E-05 0.0      0.0      0.0      0.0      0.0      1.281E-05
   1   16     10.900    9.900   0.0      3.564E-05 0.0      0.0      0.0      0.0      0.0      3.564E-05
   1   17     10.900   10.100   0.0      2.071E-05 0.0      0.0      0.0      0.0      0.0      2.071E-05
   1   18     10.900   10.200   0.0      4.191E-06 0.0      0.0      0.0      0.0      0.0      4.191E-06
   1   19     12.100    9.800   0.0      1.066E-05 0.0      0.0      0.0      0.0      0.0      1.066E-05
   1   20     12.100    9.900   0.0      1.261E-05 0.0      0.0      0.0      0.0      0.0      1.261E-05
   1   21     12.100   10.100   0.0      9.213E-06 0.0      0.0      0.0      0.0      0.0      9.213E-06
   1   22     12.100   10.200   0.0      5.668E-06 0.0      0.0      0.0      0.0      0.0      5.668E-06

 * * C O N C E N T R A T I O N S   A T    R E C E P T O R S * * *

     CONCENTRATIONS IN GRAMS PER CUBIC METER               FROM     FROM     FROM     FROM
HOUR RECEPTOR     RECEPTOR COORDINATES    FROM      FROM     HORIZONAL CURVED  SPECIAL  SPECIAL
        NO.      EAST     NORTH   HEIGHT  POINTS    AREAS    LINES    PATHS    LINES    PATHS    TOTAL


   2    1     10.500   10.000   0.0      8.167E-05 0.0      0.0      0.0      0.0      0.0      8.167E-05
   2    2     10.700   10.000   0.0      5.733E-05 0.0      0.0      0.0      0.0      0.0      5.733E-05
   2    3     10.900   10.000   0.0      4.205E-05 0.0      0.0      0.0      0.0      0.0      4.205E-05
   2    4     11.100   10.000   0.0      3.206E-05 0.0      0.0      0.0      0.0      0.0      3.206E-05
   2    5     11.300   10.000   0.0      2.523E-05 0.0      0.0      0.0      0.0      0.0      2.523E-05
   2    6     11.500   10.000   0.0      2.038E-05 0.0      0.0      0.0      0.0      0.0      2.038E-05
   2    7     11.700   10.000   0.0      1.681E-05 0.0      0.0      0.0      0.0      0.0      1.681E-05
   2    8     11.900   10.000   0.0      1.411E-05 0.0      0.0      0.0      0.0      0.0      1.411E-05
   2    9     12.100   10.000   0.0      1.202E-05 0.0      0.0      0.0      0.0      0.0      1.202E-05
   2   10     12.300   10.000   0.0      1.037E-05 0.0      0.0      0.0      0.0      0.0      1.037E-05
   2   11     12.500   10.000   0.0      9.041E-06 0.0      0.0      0.0      0.0      0.0      9.041E-06
   2   12     12.700   10.000   0.0      7.958E-06 0.0      0.0      0.0      0.0      0.0      7.958E-06
   2   13     12.900   10.000   0.0      7.062E-06 0.0      0.0      0.0      0.0      0.0      7.062E-06
   2   14     13.100   10.000   0.0      6.312E-06 0.0      0.0      0.0      0.0      0.0      6.312E-06
   2   15     10.900    9.800   0.0      4.190E-06 0.0      0.0      0.0      0.0      0.0      4.190E-06
   2   16     10.900    9.900   0.0      2.071E-05 0.0      0.0      0.0      0.0      0.0      2.071E-05
   2   17     10.900   10.100   0.0      3.565E-05 0.0      0.0      0.0      0.0      0.0      3.565E-05
   2   18     10.900   10.200   0.0      1.281E-05 0.0      0.0      0.0      0.0      0.0      1.281E-05
   2   19     12.100    9.800   0.0      5.668E-06 0.0      0.0      0.0      0.0      0.0      5.668E-06
   2   20     12.100    9.900   0.0      9.213E-06 0.0      0.0      0.0      0.0      0.0      9.213E-06
   2   21     12.100   10.100   0.0      1.261E-05 0.0      0.0      0.0      0.0      0.0      1.261E-05
   2   22     12.100   10.200   0.0      1.066E-05 0.0      0.0      0.0      0.0      0.0      1.066E-05

 * * C O N C E N T R A T I O N S   A T    R E C E P T O R S * * *

     CONCENTRATIONS IN GRAMS PER CUBIC METER               FROM     FROM     FROM     FROM
HOUR RECEPTOR     RECEPTOR COORDINATES    FROM      FROM     HORIZONAL CURVED  SPECIAL  SPECIAL
        NO.      EAST     NORTH   HEIGHT  POINTS    AREAS    LINES    PATHS    LINES    PATHS    TOTAL


   3    1     10.500   10.000   0.0      7.579E-05 0.0      0.0      0.0      0.0      0.0      7.579E-05
   3    2     10.700   10.000   0.0      5.336E-05 0.0      0.0      0.0      0.0      0.0      5.336E-05
   3    3     10.900   10.000   0.0      3.924E-05 0.0      0.0      0.0      0.0      0.0      3.924E-05
   3    4     11.100   10.000   0.0      2.998E-05 0.0      0.0      0.0      0.0      0.0      2.998E-05
   3    5     11.300   10.000   0.0      2.364E-05 0.0      0.0      0.0      0.0      0.0      2.364E-05
   3    6     11.500   10.000   0.0      1.912E-05 0.0      0.0      0.0      0.0      0.0      1.912E-05
   3    7     11.700   10.000   0.0      1.580E-05 0.0      0.0      0.0      0.0      0.0      1.580E-05
   3    8     11.900   10.000   0.0      1.328E-05 0.0      0.0      0.0      0.0      0.0      1.328E-05
   3    9     12.100   10.000   0.0      1.132E-05 0.0      0.0      0.0      0.0      0.0      1.132E-05
   3   10     12.300   10.000   0.0      9.781E-06 0.0      0.0      0.0      0.0      0.0      9.781E-06
   3   11     12.500   10.000   0.0      8.538E-06 0.0      0.0      0.0      0.0      0.0      8.538E-06
   3   12     12.700   10.000   0.0      7.522E-06 0.0      0.0      0.0      0.0      0.0      7.522E-06
   3   13     12.900   10.000   0.0      6.681E-06 0.0      0.0      0.0      0.0      0.0      6.681E-06
   3   14     13.100   10.000   0.0      5.977E-06 0.0      0.0      0.0      0.0      0.0      5.977E-06
   3   15     10.900    9.800   0.0      9.081E-06 0.0      0.0      0.0      0.0      0.0      9.081E-06
   3   16     10.900    9.900   0.0      2.907E-05 0.0      0.0      0.0      0.0      0.0      2.907E-05
   3   17     10.900   10.100   0.0      2.216E-05 0.0      0.0      0.0      0.0      0.0      2.216E-05
   3   18     10.900   10.200   0.0      5.196E-06 0.0      0.0      0.0      0.0      0.0      5.196E-06
   3   19     12.100    9.800   0.0      8.586E-06 0.0      0.0      0.0      0.0      0.0      8.586E-06
   3   20     12.100    9.900   0.0      1.099E-05 0.0      0.0      0.0      0.0      0.0      1.099E-05
   3   21     12.100   10.100   0.0      9.393E-06 0.0      0.0      0.0      0.0      0.0      9.393E-06
   3   22     12.100   10.200   0.0      6.263E-06 0.0      0.0      0.0      0.0      0.0      6.263E-06
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AVERAGE CONCENTRATIONS FOR   3 HOURS.

 **C O N C E N T R A T I O N S   A T    R E C E P T O R S***

     CONCENTRATIONS IN GRAMS PER CUBIC METER                      FROM       FROM       FROM       FROM
HOUR RECEPTOR      RECEPTOR COORDINATES     FROM        FROM      HORIZONAL  CURVED     SPECIAL    SPECIAL
        NO.      EAST      NORTH   HEIGHT   POINTS      AREAS     LINES      PATHS      LINES      PATHS      TOTAL


  0      1      10.500    10.000    0.0      7.971E-05 0.0        0.0        0.0        0.0        0.0        7.971E-05
  0      2      10.700    10.000    0.0      5.601E-05 0.0        0.0        0.0        0.0        0.0        5.601E-05
  0      3      10.900    10.000    0.0      4.111E-05 0.0        0.0        0.0        0.0        0.0        4.111E-05
  0      4      11.100    10.000    0.0      3.137E-05 0.0        0.0        0.0        0.0        0.0        3.137E-05
  0      5      11.300    10.000    0.0      2.470E-05 0.0        0.0        0.0        0.0        0.0        2.470E-05
  0      6      11.500    10.000    0.0      1.996E-05 0.0        0.0        0.0        0.0        0.0        1.996E-05
  0      7      11.700    10.000    0.0      1.647E-05 0.0        0.0        0.0        0.0        0.0        1.647E-05
  0      8      11.900    10.000    0.0      1.383E-05 0.0        0.0        0.0        0.0        0.0        1.383E-05
  0      9      12.100    10.000    0.0      1.179E-05 0.0        0.0        0.0        0.0        0.0        1.179E-05
  0     10      12.300    10.000    0.0      1.017E-05 0.0        0.0        0.0        0.0        0.0        1.017E-05
  0     11      12.500    10.000    0.0      8.873E-06 0.0        0.0        0.0        0.0        0.0        8.873E-06
  0     12      12.700    10.000    0.0      7.813E-06 0.0        0.0        0.0        0.0        0.0        7.813E-06
  0     13      12.900    10.000    0.0      6.935E-06 0.0        0.0        0.0        0.0        0.0        6.935E-06
  0     14      13.100    10.000    0.0      6.200E-06 0.0        0.0        0.0        0.0        0.0        6.200E-06
  0     15      10.900     9.800    0.0      8.695E-06 0.0        0.0        0.0        0.0        0.0        8.695E-06
  0     16      10.900     9.900    0.0      2.847E-05 0.0        0.0        0.0        0.0        0.0        2.847E-05
  0     17      10.900    10.100    0.0      2.617E-05 0.0        0.0        0.0        0.0        0.0        2.617E-05
  0     18      10.900    10.200    0.0      7.400E-06 0.0        0.0        0.0        0.0        0.0        7.400E-06
  0     19      12.100     9.800    0.0      8.304E-06 0.0        0.0        0.0        0.0        0.0        8.304E-06
  0     20      12.100     9.900    0.0      1.094E-05 0.0        0.0        0.0        0.0        0.0        1.094E-05
  0     21      12.100    10.100    0.0      1.041E-05 0.0        0.0        0.0        0.0        0.0        1.041E-05
  0     22      12.100    10.200    0.0      7.530E-06 0.0        0.0        0.0        0.0        0.0        7.530E-06




TCP OUTPUT CHARGE: $  .08
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NEW WALES NORMAL DISPERSION ANALYSIS - LOAD-OUT, NORMAL DISPERSION 24-HR PART. MATTER SION 78310
PINA =    0.02000 PINL =    0.02000

                SOURCE       WIND INCREASE
               INCLUDED      WITH  HEIGHT

    POINT        YES              NO

    AREA         NO               NO

HORIZONTAL
LINE SOURCE      NO               NO

    CURVE
PATH SOURCE      NO               NO

  SPECIAL
LINE SOURCE      NO               NO

  SPECIAL
PATH SOURCE      NO               NO          AVERAGE     YES   DIURNAL     NO     HEIGHT AT WIND SPEED   10.0 METERS


* * * P O I N T   S O U R C E S * * *
     NO.      POINT     PHYSICAL    STACK       STACK      STACK      VOLUME        COORDINATES         INITIAL SIGMAS
              SOURCE     HEIGHT      TEMP        GAS      DIAMETER     FLOW        EAST     NORTH         Y          Z
             STRENGTH   (METERS)   (DEG-K)    VELOCITY   (METERS)   (CU M/SEC)    (KM)      (KM)         (M)        (M)
              (G/SEC)                          (M/SEC)

      1         0.25       30.5      310.0      27.30       0.46        0.0      10.000    10.000        1.0        1.0

  * * R E C E P T O R S * * *

     NO.     RREC(KM)   SREC(KM)     Z (M)

       1      10.500     10.000       0.0
       2      10.700     10.000       0.0
       3      10.900     10.000       0.0
       4      11.100     10.000       0.0
       5      11.300     10.000       0.0
       6      11.500     10.000       0.0
       7      11.700     10.000       0.0
       8      11.900     10.000       0.0
       9      12.100     10.000       0.0
      10      10.900      9.800       0.0
      11      10.900      9.900       0.0
      12      10.900     10.100       0.0
      13      10.900     10.200       0.0
      14      12.100      9.800       0.0
      15      12.100      9.900       0.0
      16      12.100     10.100       0.0
      17      12.100     10.200       0.0
      18      10.900     10.000      10.0
      19      10.900     10.000      20.0
      20      10.900     10.000      30.0
      21      10.900     10.000      40.0
      22      12.100     10.000      10.0
      23      12.100     10.000      20.0
      24      12.100     10.000      30.0
      25      12.100     10.000      40.0

  * * M E T E O R O L O G Y * * *

     NO.   THETA(DEG)     U (M/SEC)     KST    HL  (M)   T (DEG-K)          DIURNAL  VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                                 HORIZONAL   CURVED     SPECIAL     SPECIAL
                                                                           POINT       AREA        LINE        PATH       LINE        PATH
      1.       228.         3.6          4      881.       296.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      2.       227.         3.1          5      954.       296.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      3.       263.         3.6          4      879.       295.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      4.       267.         3.5          4      878.       296.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      5.       259.         4.1          4      878.       297.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      6.       263.         4.1          4      877.       298.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      7.       275.         4.1          4      876.       299.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      8.       269.         3.6          4      875.       300.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
      9.       291.         4.1          4      875.       300.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
     10.       266.         4.1          4      874.       303.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
     11.       323.         5.1          4      873.       302.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
     12.       278.         3.6          4      872.       304.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
     13.       297.         4.6          4      871.       305.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
     14.       250.         6.2          4      871.       305.           1.0000      1.0000      1.0000      1.0000     1.0000      1.0000
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       15.        276.        5.7          4        870.       306.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       16.        280.        5.7          4        869.       306.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       17.        273.        5.7          4        868.       302.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       18.        294.        5.1          4        868.       300.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       19.        279.        4.1          4        867.       300.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       20.        281.        4.6          4        866.       300.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       21.        233.        4.1          4        865.       298.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       22.        238.        5.7          4        864.       298.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       23.        270.        3.6          4        864.       297.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       24.        267.        3.6          4        876.       296.            1.0000    1.0000    1.0000    1.0000    1.0000    1.0000


AVERAGE CONCENTRATIONS FOR  24 HOURS.

 * * C O N C E N T R A T I O N S   A T    R E C E P T O R S * * *

     CONCENTRATIONS IN GRAMS PER CUBIC METER                          FROM       FROM      FROM      FROM
HOUR RECEPTOR      RECEPTOR COORDINATES     FROM        FROM        HORIZONTAL CURVED    SPECIAL   SPECIAL
        NO.      EAST     NORTH   HEIGHT   POINTS      AREAS       LINES      PATHS     LINES     PATHS       TOTAL


  0      1      10.500   10.000   0.0     1.472E-06  0.0        0.0        0.0       0.0       0.0         1.472E-06
  0      2      10.700   10.000   0.0     1.578E-06  0.0        0.0        0.0       0.0       0.0         1.578E-06
  0      3      10.900   10.000   0.0     1.379E-06  0.0        0.0        0.0       0.0       0.0         1.379E-06
  0      4      11.100   10.000   0.0     1.148E-06  0.0        0.0        0.0       0.0       0.0         1.148E-06
  0      5      11.300   10.000   0.0     9.538E-07  0.0        0.0        0.0       0.0       0.0         9.538E-07
  0      6      11.500   10.000   0.0     8.028E-07  0.0        0.0        0.0       0.0       0.0         8.028E-07
  0      7      11.700   10.000   0.0     6.923E-07  0.0        0.0        0.0       0.0       0.0         6.923E-07
  0      8      11.900   10.000   0.0     5.986E-07  0.0        0.0        0.0       0.0       0.0         5.986E-07
  0      9      12.100   10.000   0.0     5.230E-07  0.0        0.0        0.0       0.0       0.0         5.230E-07
  0     10      10.900    9.800   0.0     9.375E-07  0.0        0.0        0.0       0.0       0.0         9.375E-07
  0     11      10.900    9.900   0.0     1.365E-06  0.0        0.0        0.0       0.0       0.0         1.365E-06
  0     12      10.900   10.100   0.0     1.313E-06  0.0        0.0        0.0       0.0       0.0         1.313E-06
  0     13      10.900   10.200   0.0     4.661E-07  0.0        0.0        0.0       0.0       0.0         4.661E-07
  0     14      12.100    9.800   0.0     4.914E-07  0.0        0.0        0.0       0.0       0.0         4.914E-07
  0     15      12.100    9.900   0.0     4.532E-07  0.0        0.0        0.0       0.0       0.0         4.532E-07
  0     16      12.100   10.100   0.0     5.997E-07  0.0        0.0        0.0       0.0       0.0         5.997E-07
  0     17      12.100   10.200   0.0     5.536E-07  0.0        0.0        0.0       0.0       0.0         5.536E-07
  0     18      10.900   10.000  10.00    1.400E-06  0.0        0.0        0.0       0.0       0.0         1.400E-06
  0     19      10.900   10.000  20.00    1.438E-06  0.0        0.0        0.0       0.0       0.0         1.438E-06
  0     20      10.900   10.000  30.00    1.439E-06  0.0        0.0        0.0       0.0       0.0         1.439E-06
  0     21      10.900   10.000  40.00    1.353E-06  0.0        0.0        0.0       0.0       0.0         1.353E-06
  0     22      12.100   10.000  10.00    5.175E-07  0.0        0.0        0.0       0.0       0.0         5.175E-07
  0     23      12.100   10.000  20.00    5.012E-07  0.0        0.0        0.0       0.0       0.0         5.012E-07
  0     24      12.100   10.000  30.00    4.747E-07  0.0        0.0        0.0       0.0       0.0         4.747E-07
  0     25      12.100   10.000  40.00    4.394E-07  0.0        0.0        0.0       0.0       0.0         4.394E-07




TCP OUTPUT CHARGE: $  .35
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NEW WALES DOWNWASH ANALYSIS - LOAD-OUT, DOWNWASH                                          VERSION 78310
PINA =    0.02000 PINL =    0.02000
                SOURCE      WIND INCREASE
               INCLUDED     WITH  HEIGHT
   POINT         YES               NO

   AREA          NO                NO

HORIZONTAL
LINE SOURCE      NO                NO

   CURVE
PATH SOURCE      NO                NO

  SPECIAL
LINE SOURCE      NO                NO

  SPECIAL
PATH SOURCE      NO                NO          AVERAGE     YES   DIURNAL     NO     HEIGHT AT WIND SPEED   10.0 METERS


* * * P O I N T   S O U R C E S * * *
      NO.     POINT     PHYSICAL    STACK       STACK      STACK     VOLUME        COORDINATES         INITIAL  SIGMAS
              SOURCE     HEIGHT     TEMP         GAS      DIAMETER    FLOW       EAST      NORTH         Y          Z
             STRENGTH   (METERS)   (DEG-K)    VELOCITY    (METERS)  (CU M/SEC)   (KM)       (KM)        (M)        (M)
              (G/SEC)                          (M/SEC)

      1         0.25       30.5      310.0       1.00        0.46       0.0     10.000     10.000       14.5       14.5

 * * R E C E P T O R S * * *

      NO.     RREC(KM)  SREC(KM)    Z (M)

        1     10.500    10.000      0.0
        2     10.700    10.000      0.0
        3     10.900    10.000      0.0
        4     11.100    10.000      0.0
        5     11.300    10.000      0.0
        6     11.500    10.000      0.0
        7     11.700    10.000      0.0
        8     11.900    10.000      0.0
        9     12.100    10.000      0.0
       10     10.900     9.800      0.0
       11     10.900     9.900      0.0
       12     10.900    10.100      0.0
       13     10.900    10.200      0.0
       14     12.100     9.800      0.0
       15     12.100     9.900      0.0
       16     12.100    10.100      0.0
       17     12.100    10.200      0.0

 * * M E T E O R O L O G Y * * *

      NO.   THETA(DEG)     U (M/SEC)     KST     HL (M)   T (DEG-K)          DIURNAL VARIATIONS (FRACTIONS OF GIVEN Q)
                                                                                          HORIZONTAL   CURVED    SPECIAL    SPECIAL
                                                                           POINT     AREA     LINE       PATH      LINE       PATH
       1.        228.          3.6           3       801.      296.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       2.        227.          3.1           3       954.      296.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       3.        263.          3.6           3       879.      295.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       4.        267.          3.6           3       878.      296.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       5.        259.          4.1           3       878.      297.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       6.        263.          4.1           3       877.      298.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       7.        275.          4.1           3       876.      298.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       8.        269.          3.6           3       875.      300.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
       9.        291.          4.1           3       875.      300.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      10.        266.          4.1           3       874.      303.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      11.        323.          5.1           3       873.      302.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      12.        278.          3.6           3       872.      304.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      13.        287.          4.6           3       871.      305.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      14.        250.          6.2           3       871.      305.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      15.        276.          5.7           3       870.      306.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      16.        260.          5.7           3       869.      306.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      17.        278.          5.7           3       868.      302.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      18.        294.          5.1           3       868.      300.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      19.        279.          4.1           3       867.      300.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      20.        281.          4.6           3       866.      300.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      21.        233.          4.1           3       865.      298.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
      22.        238.          5.7           3       864.      298.        1.0000    1.0000    1.0000    1.0000    1.0000    1.0000
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        23.       270.       3.6        3     864.      297.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000
        24.       267.       3.6        3     976.      296.          1.0000   1.0000   1.0000   1.0000   1.0000   1.0000


AVERAGE CONCENTRATIONS FOR  24 HOURS.

 * * C O N C E N T R A T I O N S   A T   R E C E P T O R S * * *

    CONCENTRATIONS IN GRAMS PER CUBIC METER                     FROM       FROM      FROM      FROM
HOUR RECEPTOR     RECEPTOR COORDINATES      FROM        FROM     HORIZONAL  CURVED    SPECIAL   SPECIAL
        NO.      EAST     NORTH    HEIGHT    POINTS      AREAS    LINES      PATHS     LINES     PATHS      TOTAL


  0      1     10.500   10.000    0.0      2.295E-06 0.0       0.0        0.0       0.0       0.0        2.295E-06
  0      2     10.700   10.000    0.0      1.462E-06 0.0       0.0        0.0       0.0       0.0        1.462E-06
  0      3     10.900   10.000    0.0      1.007E-06 0.0       0.0        0.0       0.0       0.0        1.007E-06
  0      4     11.100   10.000    0.0      7.347E-07 0.0       0.0        0.0       0.0       0.0        7.347E-07
  0      5     11.300   10.000    0.0      5.592E-07 0.0       0.0        0.0       0.0       0.0        5.592E-07
  0      6     11.500   10.000    0.0      4.398E-07 0.0       0.0        0.0       0.0       0.0        4.398E-07
  0      7     11.700   10.000    0.0      3.551E-07 0.0       0.0        0.0       0.0       0.0        3.551E-07
  0      8     11.900   10.000    0.0      2.928E-07 0.0       0.0        0.0       0.0       0.0        2.928E-07
  0      9     12.100   10.000    0.0      2.456E-07 0.0       0.0        0.0       0.0       0.0        2.456E-07
  0     10     10.900    9.800    0.0      6.751E-07 0.0       0.0        0.0       0.0       0.0        6.751E-07
  0     11     10.900    9.900    0.0      9.169E-07 0.0       0.0        0.0       0.0       0.0        9.169E-07
  0     12     10.900   10.100    0.0      8.394E-07 0.0       0.0        0.0       0.0       0.0        8.394E-07
  0     13     10.900   10.200    0.0      4.622E-07 0.0       0.0        0.0       0.0       0.0        4.622E-07
  0     14     12.100    9.800    0.0      2.271E-07 0.0       0.0        0.0       0.0       0.0        2.271E-07
  0     15     12.100    9.900    0.0      2.389E-07 0.0       0.0        0.0       0.0       0.0        2.389E-07
  0     16     12.100   10.100    0.0      2.419E-07 0.0       0.0        0.0       0.0       0.0        2.419E-07
  0     17     12.100   10.200    0.0      2.202E-07 0.0       0.0        0.0       0.0       0.0        2.202E-07




TCP OUTPUT CHARGE: $  .28
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10.0 IMPACT OF FLUORIDE EMISSIONS

Fluorides in ambient air have been defined by EPA to be a welfare related pollutant as opposed to a health related pollutant(1). This is to say that fluoride levels as observed in the ambient air in the U.S. have not caused any health related effects. Effects on non-human receptors have been noted however.

When fluorides are emitted into the atmosphere in large volumes they have a tendency to accumulate in various types of vegetation and in some cases cause damage to the vegetation. A secondary effect of the accumulation of fluorides in vegetation occurs when vegetation is consumed by foraging animals. If the animals consume sufficient quantities of the fluoride, damage to teeth and bones, known as fluorosis, can occur.

In the phosphate fertilizer industry all point sources of fluorides have been controlled for quite some time. As the result of this, welfare related effects have virtually been non-existent. In 1978 an Environmental Impact Statement was prepared to describe the environmental effects of a proposed phosphate fertilizer plant expansion(2). One phase of the EIS involved investigating the effects of fluorides on the environment surrounding the existing plant. The section of the EIS dealing with the observed fluoride effects are included in this document as Section 1.0, Attachment 4.

At the time this study was conducted, the existing fertilizer plant which was the subject of the study, had a capacity of 550,000 tons per year of P_2O_5. A description of the plant is included in Section 1.0, Attachment 4.

The existing New Wales Chemical Complex has a capacity of approximately 900,000 tons per year of P_2O_5. This is approximately 65 percent larger than the phosphate fertilizer complex referenced in Section 1.0, Attachment 4.

Prior to the construction of the initial New Wales Chemical Complex in 1975 and for four years following the initial plant start-up, the New Wales Chemical Company measured fluoride levels in the ambient air, in citrus leaves and in grass (Section 1.0, Attachment 2). The results of this study by New Wales showed fluoride levels somewhat higher than those referenced in the Section 1.0, Attachment 4. It should be noted; however, that the fluoride levels measured by New Wales in ambient air and in the foliage samples did not increase after the plant began operation. It must be concluded that the fluoride levels measured around the New Wales Chemical Complex result primarily from other phosphate related activities in the same general area.

New Wales has received no complaints of damage to cattle, citrus or other crops as a result of fluoride emissions from their existing facility. It is not anticipated that the 26 tons per year increase in fluoride emissions resulting from the proposed phosphoric acid and DAP plants and the increased cooling pond emissions will cause this to change.

REFERENCES
SECTION 10

1. Final Guideline Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants, EPA-450/2-77-005, USEPA, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, March 1977.

2. Environmental Impact Statement, Occidental Chemical Company Swift Creek Chemical Complex, Hamilton County, Florida, EPA 904/9-78-012-A, USEPA, Region IV, Atlanta, Georgia, July 1978.

11.0 SECONDARY IMPACTS FROM MOBILE SOURCES

In this section the secondary impacts of mobil sources on ambient air quality are addressed.

Under present operating conditions, New Wales employs approximately 850 persons. Automobile traffic generated by these employees results in approximately 400 automobile trips to and from the plant each day. In addition to this traffic, there are approximately 300 truck trips and 225 rail car trips to and from the plant on a typical day.

The expansion proposed by New Wales will result in approximately 300 new employees and will require an additional 150 trucks per day and 75 additional rail cars per day.

The additional automobile traffic and truck traffic will result in approximately 432,000 vehicle miles traveled per year on New Wales property. This distance was calculated by considering vehicle travel from SR 640 approximately one mile north of the plant to the plant site and returning to SR 640.

Using EPA emission factors from AP-42 it was calculated that the additional traffic will generate the following pollutant burdens:

Carbon monoxide - 36.4 tons per year
Nitrogen oxides - 2.3 tons per year
Hydrocarbons - 5.1 tons per year
Part. Matter - 2.9 tons per year.

Considering the fact that these pollutants will be emitted as a line source approximately one mile long, the impact on air quality will not be significant.