

**Bull, Robert**

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**From:** Linero, Alvaro  
**Sent:** Thursday, March 17, 2005 8:21 PM  
**To:** Bull, Robert  
**Cc:** Pichard, Errin; Pennington, Jim; Vielhauer, Trina  
**Subject:** RE: Mosaic South Pierce HF Pond Testing Protocol

Thanks Bobby.

Actually Trina or Vicky gave me a copy of the report.

They will use the top person in the field. Dr. Hashmonay is top dog (maybe in the world) in testing of emissions from surfaces, tomography, OP-FTIR. Among his credits is the characterization of practically every large swine lagoon in the country (on behalf of EPA) for ammonia emissions. He has developed and refined the techniques that EPA and the Air Force claim is the correct way of doing these things.

I happen to be No. 1 in the country (among government bureaucrats!) in this specific issue having published a key report and also presented a paper at AWMA in San Diego in 2003. A courtesy copy is attached. You can see my credit to Hashmonay in the acknowledgements. What MOSAIC is doing is exactly what I recommended in the paper under conclusions.

I don't think there is much to criticize in the work he will do. I would like to personally ask him one or two questions, but not turn it into a number of RAI type exercises that could put off the work into the hurricane season.

What we need to do is to get concurrent data during the time of the tests on process production, pond water flows, temperature if possible, fluoride concentration, silica, pH, K, Na and maybe a few other parameters. The key is to make sure the pond they will use is and has been in use recently and is not a "dead" pond as far as HF evolution is concerned. See page 6 of the paper for the types of parameters we need.

I think the best thing to do is tell them we agree with the protocol, but that we would like to be present at the project kick off meeting and the testing and want access to the process data.

I recommend we call Phil Steadham and discuss these things.

Cargill and IMC (Now MOSAIC) made a big error when they did similar testing over ten years ago. I'm the person who caught it. Best if you let me get this one off the tarmac and then hand the controls over to you while I parachute out. Better than me discovering some fatal flaw in a few years.

If emissions are low, they might claim they speak for all ponds. That's why I want the process info without delaying the tests.

We need to identify a team. That could include someone over in monitoring area, maybe someone from DEP Labs, SWD, etc.

This is actually a very exciting project.

O.k. Thanks.

Al.

3/18/2005

-----Original Message-----

**From:** Bull, Robert  
**Sent:** Thu 3/17/2005 12:51 PM  
**To:** Vielhauer, Trina; Pennington, Jim; Pichard, Errin  
**Cc:** Linero, Alvaro  
**Subject:** RE: Mosaic South Pierce HF Pond Testing Protocol

Al, I'll have a copy of the proposal to you today.

-----Original Message-----

**From:** Vielhauer, Trina  
**Sent:** Thursday, March 17, 2005 12:50 PM  
**To:** Bull, Robert; Pennington, Jim; Pichard, Errin  
**Cc:** Linero, Alvaro  
**Subject:** RE: Mosaic South Pierce HF Pond Testing Protocol

Bobby,

Can you also discuss it with Al? He's been involved in the phosphate MACT issue [especially the pond issues] for a long time and has a lot of insight on this. Thank you,

Trina

-----Original Message-----

**From:** Bull, Robert  
**Sent:** Wednesday, March 16, 2005 7:53 AM  
**To:** Vielhauer, Trina; Pennington, Jim; Pichard, Errin  
**Subject:** Mosaic South Pierce HF Pond Testing Protocol

Good Morning,

Yesterday we received a copy of the proposed pond testing protocol from Mosaic South Pierce. Arcadis will be conducting the testing. I have a copies made for review and will get them to you today.

Thanks

# Hydrogen Fluoride Emissions from Phosphoric Acid Process Ponds

Paper # 69816

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## ABSTRACT

Hydrogen fluoride (HF) is the main hazardous air pollutant (HAP) emitted from phosphoric acid and fertilizer manufacturing facilities. The U.S. EPA developed two NESHAP regulations (40 CFR 63, Subparts AA and BB) applicable to these facilities. A number of major manufacturers have advised that Subparts AA and BB do not apply to their facilities because emissions of HF from the processes and fugitive sources, such as process ponds, are less than 10 tons per year. Because these facilities process phosphate rock containing on the order of 50,000 to 150,000 TPY of fluorides, it is important to explore the fate of fluorides and determine the potential for emissions of HF. This paper reviews the present status of the issue with special emphasis on the potential for emissions from the highly acidic process ponds.

## INTRODUCTION

There has been intermittent interest in fluoride emissions from phosphoric acid gypsum and cooling ponds (process ponds) since the 1960's. After establishing fluoride control requirements for process emission sources under the New Source Performance Standards (NSPS) in the early 1970's, EPA hypothesized that the process ponds are the greatest remaining potential sources of fluoride emissions. A number of studies were conducted, but no rules were promulgated.

The 1990 Clean Air Act Amendments classified hydrogen fluoride HF as a HAP under Title III. In 1999, EPA promulgated National Emission Standards for Hazardous Air Pollutants (NESHAP's) for the phosphoric acid and fertilizer industries at 40 CFR 63, Subparts AA and BB.<sup>1</sup> EPA estimated that HF emissions from all phosphoric acid and fertilizer facilities nationwide would be reduced from 605 tons per year to 260 TPY by implementation of Maximum Achievable Control Technology (MACT) under Subparts AA and BB. EPA required control of fluoride as the surrogate for HF emissions from process emission units. EPA required no control for process ponds.

Recently some of the largest phosphoric acid/fertilizer companies in the country claimed that total emissions of HF from process stacks and process ponds are minimal to the extent that their facilities are actually minor sources of HAPs and not subject to Subparts AA or BB.

This review reexamines the magnitude of HF emissions from the process ponds. These must be aggregated with emissions from the process stacks in making major HAPs source applicability determinations. The review is not a reexamination of EPA and industry conclusions regarding HF emissions from process emission units but the need for such a review is obvious.

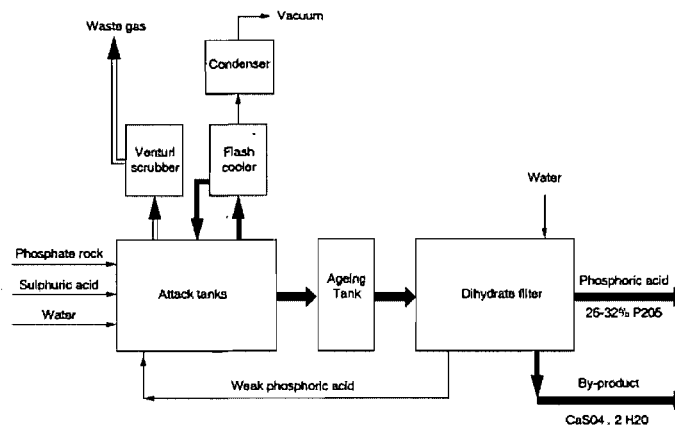
## BASIC PHOSPHORIC ACID PROCESS DESCRIPTION

According to EPA's rule summaries, there were 47 wet acid plants at 21 locations. Plants in Florida produce more than half of all phosphoric acid produced in the United States.

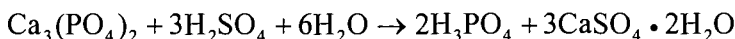
The key mineral in phosphate rock is fluorapatite  $[\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2]$ . Fluorapatite from Florida contains roughly 34 percent (%)  $\text{P}_2\text{O}_5$  by weight, 50%  $\text{CaO}$ , 3.9% fluoride (F), 3.7 % silica ( $\text{SiO}_2$ ), and 3.1%  $\text{CO}_2$ .<sup>2</sup> The silica can vary greatly and affects the ultimate fate of fluorides. There is also carbon (3.1% as  $\text{CO}_2$ ) and varying amounts of iron (Fe), aluminum, (Al), sodium (Na), potassium (K), and magnesium (Mg) at levels less of 1% by weight or less.

Sulfuric acid (produced on site or imported), phosphate rock and water are reacted in an attack tank with one another to produce phosphoric acid and byproduct gypsum. Following is a simplified flow diagram for the dihydrate variation of the wet phosphoric acid manufacturing process.

**Figure 1.** Dihydrate Wet Process Phosphoric Acid Process Flow Diagram (Source: EFMA)

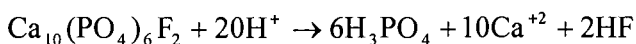


**Equation 1.** According to Becker, the tricalcium phosphate component of the fluorapatite reacts with sulfuric acid to produce phosphoric acid as follows:<sup>3</sup>



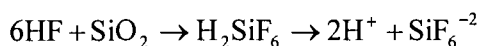
Depending on operating temperature, the crystallized  $\text{CaSO}_4$  (gypsum) formed by the reaction can be in the dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) form per Equation 1 or the hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) form. For reference all but one company in Florida use the lower temperature (70-80 degrees °C) dihydrate wet process as opposed to the higher temperature (90-110°C) hemihydrate process. Acidulation of fluorapatite also releases the entire fluorine component.

**Equation 2.** Prior to crystallization of gypsum, hydrofluoric acid (HF) is produced in the highly acidified environment in accordance with the following simplified equation:



HF in the environment of the attack tank is a weak acid with a strong tendency to react with silica that is present to varying degrees to form fluosilicic acid that in turn dissociates to fluosilicate ions.

**Equation 3.** The reactions are as follows:

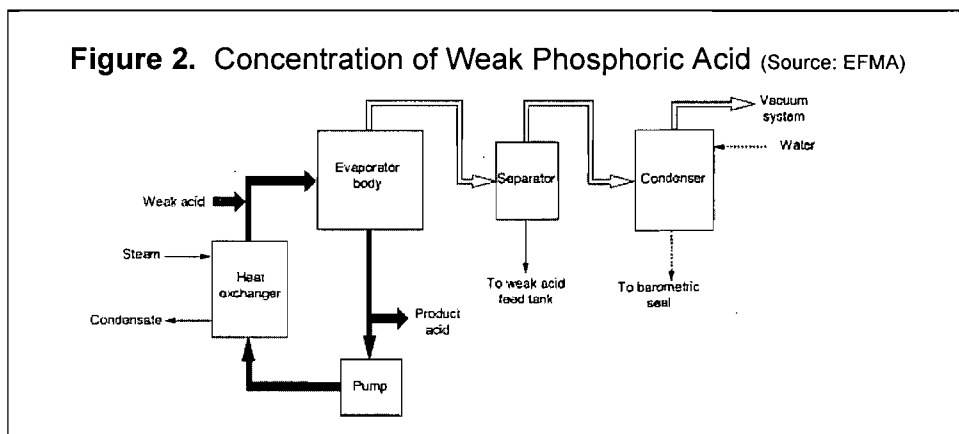


**Equation 4.** Some fluosilicic acid can also break down into its gaseous components that exert vapor pressure within the slurry and leave with cooling air or vacuum cooling water as follows:



The product of the initial acidulation is filtered in one or more “tilting pan” cloth filters to separate the nominal 30 percent weak phosphoric acid (WPA) from byproduct gypsum. The separated gypsum falls as each pan section is sequentially tilted. It is then pumped as slurry to ponds atop stacks of waste gypsum where the solids settle and decanted liquids are combined with process cooling water and returned to the process.

The weak phosphoric acid is typically further concentrated by evaporation to roughly 50 percent phosphoric acid (as  $\text{P}_2\text{O}_5$ ). Figure 2 is a flow diagram of this process step. Typically it is performed in three stages yielding concentrations of roughly 37, 45, and 52 percent as  $\text{P}_2\text{O}_5$ . These steps provide additional opportunities for further evolution of HF and  $\text{SiF}_4$ .



## FLUORIDE DISTRIBUTION WITHIN THE PROCESS

The product phosphoric acid can be further processed to make superphosphoric acid, ammonium phosphates (MAP and DAP), granular triple super phosphate (GTSP), defluorinated calcium phosphates (animal feed), etc. Discussion of phosphoric acid manufacturing is sufficient to gain an appreciation of the sources and fate of fluorides as well as their potential for evolution as hazardous air pollutants.

Of major concern here is the fate of fluorides present in the raw materials. For the purposes of discussion it is assumed that a large facility can make approximately 4000 tons per day of phosphoric acid (as  $\text{P}_2\text{O}_5$ ). Such a plant would require a little less than 12,000 tons per day of phosphate rock on a dry basis. This is in approximate agreement with values in a recent application by an operator in Florida.<sup>4</sup>

The amount of fluoride flowing through such a facility is, based on 3.9 tons F/100 tons rock, on the order of 170,000 TPY. Assuming some down time and less than maximum operating rates, it is reasonable to conclude that roughly 150,000 TPY of fluorides enter the “model” plant. A typical fluorine distribution in the dihydrate process is given in Table 1:

**Table 1.** Fluorine Distribution in 4000 TPD Dihydrate Process (percentages per EFMA)

Distribution	Percent	Tons Per Year Fluoride
Acid	15	22,500
Phosphogypsum	43	64,500
Reactor off-gas	5	7,500
Flash cooler vapor	2	3,000
Concentrator vapor	35	52,500

This “typical distribution” can be greatly affected by presence of silica, recovery of fluosilicic acid, and numerous other factors. However it is a reasonable starting point for further discussion.

Much of the fluoride component stays in the weak phosphoric acid during initial acidulation.  $\text{SiF}_4$  is preferentially volatilized because under the conditions prevailing in the reactor its vapor pressure is higher than that of HF. The molar ratio HF: $\text{SiF}_4$  in the vapors increases sharply with the concentration of the phosphoric acid and surpasses 2:1 when the acid concentration is 50%  $\text{P}_2\text{O}_5$  or more.<sup>5</sup>

Assuming that the off-gases are scrubbed to recover fluosilicic acid or absorbed using pond water via barometric condensers serving the evaporators, there should be “relatively low” emissions of gaseous fluorides compared with total fluoride flows (measured in tens of thousands of TPY) within the process. However such emissions can easily be relatively “high” compared with HAPs major source thresholds (10 TPY of HF).

## PROCESS PONDS

Gypsum cake separated from weak phosphoric acid is slurried with water from process cooling ponds and conveyed to an area atop a very large stack of waste gypsum. The solids from the slurry settle and decanted water moves across to other areas on or around the gypsum stack that hold cooling water. There are many arrangements and degrees to which cooling and gypsum pond waters are mixed or segregated. For the purposes of further discussion it will be assumed that a 4000 TPD  $\text{P}_2\text{O}_5$  has approximately a 640-acre pond (one square mile). Figure 3 is an aerial view of one process pond system that could easily occupy one square mile.<sup>6</sup>

Based on Table 1 and assuming that the facility makes only phosphoric acid, approximately 120,000 TPY of fluoride may be permanently “fixed” within the pond environment. This necessarily means that this amount must ultimately precipitate as solids with the exception of fluorides that are recovered as byproduct fluosilicic acid or even sodium fluoride.

**Figure 3.** Aerial View of a Process Pond System in Florida



There are quite a number of solid fluoride compounds in the gypsum slurry or in sludge generated during the concentration of weak phosphoric acid. The key fluoride containing compounds identified in one reference are listed in the following table:

**Table 2.** Solid Fluorine Compounds Capable of Forming (source: Becker)

Compound	Formation, Comment
$\text{Na}_2\text{SiF}_6$ , $\text{K}_2\text{SiF}_6$ , $\text{NaKSiF}_6$	Slurry cooling, scale forming
$\text{CaSO}_4\text{CaSiF}_6\text{CaAlF}_6(\text{Na}) \cdot 12\text{H}_2\text{O}$	Chukrovite, nuisance during filtration
$\text{CaF}_2$	Fluorspar, precipitates during concentration
$\text{MgAlF}_6\text{Na} \cdot 6\text{H}_2\text{O}$	Ralstonite, precipitates during concentration

Although the fate of fluorides is primarily as the solids described above, at any given time there is a reservoir of fluorides and other species in the liquid environment of the process pond system including the recirculating streams used in the scrubbers and condensers. Following are average pooled process water constituents from six different pond systems.<sup>7</sup>

**Table 3.** Average Percent (% by wt) Concentrations of Components in Process Pond Systems

Component	Plant to Pond (%)	Pond to Plant (%)	Slurry Filtrate (%)
P <sub>2</sub> O <sub>5</sub>	1.50	1.57	1.70
F	0.793	0.790	0.832
S (SO <sub>4</sub> )	0.163	0.175	0.172
Si	0.206	0.203	0.202
Al	0.018	0.019	0.021
Ca	0.126	0.128	0.131
Fe	0.023	0.021	0.025
K	0.031	0.027	0.029
Mg	0.024	0.028	0.029
Na	0.185	0.184	0.211
N (NH <sub>4</sub> )	0.077	0.063	0.074
Cl	0.034	0.020	0.017
pH	pH = 1.72	pH = 1.67	pH = 1.71

The slate above is reported according to an industry convention. Thus F represents fluorine in its many forms including fluosilicates, complex iron and aluminum fluoride ions, HF, etc. As expected, P<sub>2</sub>O<sub>5</sub> (forms of phosphoric acid) is the species of greatest concentration. Fluorides are present in high concentration. Silicon is also present in high concentration, largely in conjunction with fluorides as fluosilicates. The pond systems are characterized by low pH.

The key question is whether significant emissions of HF can occur over the time and area between the introduction of gypsum slurry and process water to the pond system and the return of such water to the process for slurrying, cooling/condensation, and scrubbing. It is noteworthy that the water entering the pond system comes from an environment where there is a net driving force towards absorption of fluorides into the water. That driving force is immediately relieved by upon exposure of this warm, fluoride-laden, low pH water to a surface area on the order of a square mile and meteorological conditions.

While much of the fluoride continues to precipitate in the process pond system as previously described, the system will seek to relieve itself of fluorides via all available channels. Thus the possibility is not far-fetched that at least 10 TPY of HF (out of 150,000 TPY of F entering the facility) will be emitted from the process pond system.



## FLUORIDE EMISSIONS ESTIMATES FROM PROCESS PONDS

There have been a number of investigations to determine fluoride emissions from phosphoric acid process ponds. Estimates from the published documents available to the author are listed below together with an unpublished document prepared by Radian for The Fertilizer Institute (Radian) and an unpublished document from the U.S. EPA (EPA/TRC). All included experimental techniques with the exception of EPA/ES&E, Moore, and Becker. The author used the emission factors developed by the respective investigators to estimate annual emissions based on the "model" 4000 TPD facility with a one square mile process pond system.

**Table 4.** Experimental Fluoride Emission Factors and Annual Emissions for a 640-Acre Pond

Investigators	Year	lb F/acre-day	Annual TPY	Comments
Cross & Ross <sup>8</sup>	1969	0.16	19	Minimum per authors
PHS/MCA AP-57 <sup>9</sup>	1970	0.4 – 2	47 - 230	Conservative per authors
Tatera Thesis <sup>10</sup>	1970	0.13 – 18.3	?	Summary from abstract
EPA/King Thesis <sup>11</sup>	1974	~ 0.7 - 7	285 – 358	0.39 to 0.49 lb/ton P <sub>2</sub> O <sub>5</sub>
EPA/ES&E <sup>12</sup>	1976	0.1 – 10	12 - 1170	EPA funded assessment
EPA/TRC <sup>13</sup>	1977	4 - 10	467 - 1170	Summary from abstract
Moore Paper <sup>14</sup>	1987	1 – 1.7	120 - 200	Analogy to H <sub>2</sub> O evaporation
Becker Text <sup>15</sup>	1989	4.6	540	Analogy to H <sub>2</sub> O evaporation
Radian <sup>16</sup>	1994	0.012 – 0.092	1.4 - 11	From report summary
Terra Air & Boreal <sup>17</sup>	1998	Not Reported	?	To determine HF/SiF <sub>4</sub>

Within the published Cross & Ross paper, the author stated their emission factor of 0.16 lb/acre-day is the minimum. The subsequent Public Health Service/Manufacturing Chemists' Association document (AP-57), alluded to the statement in the Cross & Ross paper. The AP-57 authors further noted that the soluble fluoride concentration in the pond studied by Cross & Ross was only 4000 ppm compared with about 10,000 ppm in the pond studied in AP-57.

The AP-57 field based estimates ranged from approximately 0.4 to 2 lb/acre-day for pond temperatures between 50 and 75 degrees Fahrenheit and 5 mile per hour wind speed. The authors state that "at the given wind speed and with reasonable vertical mixing of air above the pond, (fluoride evolution) is probably somewhat greater than indicated by the curve." Furthermore, it is very likely that emissions will be greater at temperatures greater than 75 degrees.

The Tatera Thesis estimates represent short-term factors derived by laboratory experiments conducted under a wide range of conditions. Since the extreme conditions giving rise to the highest and lowest values are not persistent, it is more likely that annualized emission factor ranges will be much more narrow. The low end of such an annualized range would certainly be greater than the Cross & Ross emission factor.

The EPA-supported King Thesis developed short-term (wide range) emission factors in terms of lb/acre-day. He also developed narrow range factors in terms of lb/ton of  $P_2O_5$ . The annual emissions given in the table are based on the latter technique.

The EPA-supported ES&E study was largely a literature search and critique of previous studies as well as a review of possible control techniques available at the time. The report included a range that covered the full range of estimates given in the previously mentioned studies. It included some theoretical considerations and a description for a possible field effort to more accurately determine fluoride emissions from ponds.

EPA subsequently contracted with TRC to conduct the field effort described by ES&E, which resulted in estimates of 4 to 10 lb/acre-day at one facility. The report also describes variability in fluoride concentration with respect to height and a "cap" at roughly 25 meters.

In his paper, Moore reviewed the estimates of Cross & Ross, AP-57, and Tatera. He provided his own theoretically derived estimate based on an analogy with evaporation of water.

In his renowned industry textbook, Becker alluded to the Tatera study and similar efforts in Germany resulting in even greater emission estimates. Becker performed his own estimate given above based on an analogy with evaporation of water.

The unpublished Radian study has been used by the industry in recent years as the basis for estimating emissions reported in the Toxic Release Inventory (TRI). It replaced the already "conservative" Cross & Ross study previously used by a number of companies. The Radian report is discussed in detail in the next section.

The Terra Air & Boreal Study utilized Fourier Transform Infrared (FTIR) and Tunable Laser Diode (TDL) measurements. The purpose was to determine the relative percentages of HF and  $SiF_4$  in total fluoride emissions from the ponds because the ambient air quality standards given in the applicable permits are specific to HF.

The authors of the Terra/Boreal Study did not estimate an emission factor. Basically the study found that emissions are primarily HF from aqueous pond surfaces. The study also concluded that that  $SiF_4$  clearly made up a significant portion of the phosphogypsum storage area fluoride emissions. S.F. Phosphates used the results in conjunction with other techniques to obtain a permit to expand the facility. The information was also used to conclude that their facility in Wyoming is a major source of HF emissions and thus subject to the applicable NESHAP's.<sup>18</sup>

## **COMPANY ESTIMATES**

During 2002, several large companies provided notification that their facilities are not subject to the industry NESHAP and MACT provisions. Fluoride and HF emission estimates submitted for certain facilities are listed in the following table:

**Table 5.** Company Fluoride and Hydrogen Fluoride Emission Estimates (F/HF) in TPY.

Facility	PhosAcid	Products	Fugitive	Ponds	Total
Facility 1	10/0.1	31.3/1.7	?/0.1	?/1.7	41/3.5
Facility 2	10/0.1	93/7.5	?/0.1	?/1.0	103/8.7
Facility 3	?/?	?/?	?/?	?/?	?/3.6
Facility 4	15/0.8	80.9/4.1	0.6/0.2	?/1.8	97/6.9
Facility 5	4.8/0.7	82/4.6	27/1.1	?/1.1	114/7.5
Facility 6	15/0.2	11.8/3.0	?/?	?/2.7	118/5.9

Because each company categorized its emissions differently, the above table format is suitable for approximate rather than exact comparison. Efforts were made to separate out the basic concentrated phosphoric acid process from products including fertilizers and superphosphoric acid. Some companies included fugitive emissions within the respective processes.

All of the values for annual HF emissions given in Table 5 are less than 10 tons per year. The result was that none of the facilities listed agreed they are major sources of HAPs. By comparison, the States of Wyoming and North Carolina issued unchallenged permits to other facilities requiring compliance with Subparts AA and BB.<sup>19,20</sup>

There are two matters of great importance in Table 5. The first is the apparently very low proportion of HF to fluoride reported by the companies. For example, HF was reported as only 1 percent of fluoride emissions from the phosphoric acid plants at facilities 1 and 2. This issue is beyond the scope of this paper and merits a separate analysis.

With purportedly low HF emissions from the stacks, the issue of emissions from the ponds looms important with respect to applicability of Subparts AA and BB. All of the companies submitted pond emission estimates weighted towards the lowest emission factor from the Radian Report (i.e. closer to 0.012 than 0.092 lb/acre-day). This issue is examined in the present paper.

## **REVIEW OF BASIS FOR INDUSTRY POND EMISSION ESTIMATES**

Radian measured HF and SiF<sub>4</sub> concentrations at two facilities on behalf of The Fertilizer Institute (TFI) using an FTIR open path spectrometer coupled with a meteorological sensing station. Measurements were made adjacent to and down-wind of ponds at an elevation of ~3-4 meters above pond surface. Measurements over the water at approximately 1 meter above the pond were made under winter conditions. Following is a summary table of measurement results.

**Table 6.** Field Measurement Summary (in ppb) Summer/Winter Conditions

Site	Max. SiF <sub>4</sub>	Mean SiF <sub>4</sub>	Min SiF <sub>4</sub>	Max HF	Mean HF	Min HF
Pond 1 (Summer)	3	0.5	0	100	57.7	22
Pond 2 (Summer)	0	0	0	81	23.2	2
Pond 2 (Winter)	(a)	(a)	(a)	35	6.7	0
Pond 2 (Winter,b)	0	0	0	28	15.6	7

(a) Measurement not made

(b) Measurement above pond surface

Data from the field measurements were also used to estimate emission rates for the two facilities by two preliminary modeling approaches: back-calculation from an analytical emission rate model; and forward-calculation using a pond chemical modeling/mass-transport model. The following table is a summary of Radian's chemical and analytical modeling techniques for HF.

**Table 7.** Preliminary Modeled HF Emissions Estimates in lb/acre-day

Site	Chemical Model Emission Rate	Analytical Model Emission Rate
Pond 1 (S)	0.018	0.092
Pond 2 (S)	0.013	0.012
Pond 2 (W)	0.015	0.012

At first glance, Radian's emission factors appear to be outliers (on the low end) compared with the other estimates given in Tables 4 above. Interestingly the measured concentrations given in Table 6 are on the same order of magnitude as concentrations measured by several other investigators who calculated emissions rates orders of magnitude greater than calculated by Radian. These facts suggest the possibility of systematic errors in the Radian report.

**Equation 5.** Radian's analytical model is based on the following equation:

$$ER = MW_{HF} C_{HF} \rho_{air} D_b \pi / 4 \tau (10^9)$$

Where:

ER = emission rate in  $\mu\text{g HF}/\text{m}^2/\text{second}$

$C_{HF}$  = concentration in ppm (of HF)

$\rho_{air}$  = number density of air in moles/ $\text{m}^3$

$D_b$  = diameter of optical beam in m

$\tau$  = average time for air parcel to travel over pond in seconds (fetch)

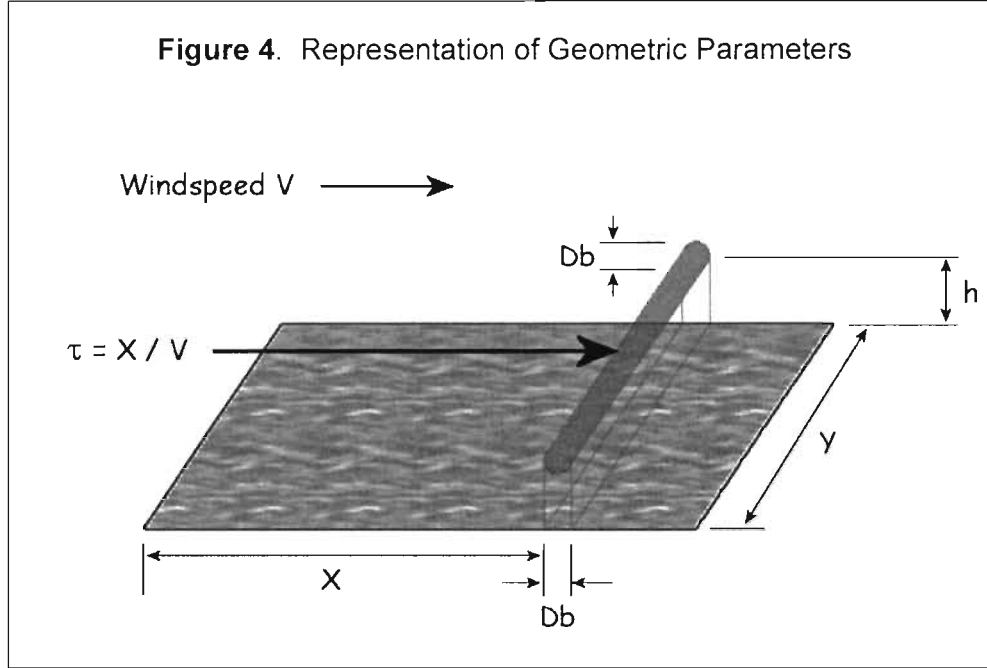
$MW_{HF}$  = molecular weight of species (HF) in grams/mole

The term " $\tau$ " is the distance the air parcel traveled over the pond (X in meters) divided by the wind speed in m/s. Thus  $\tau = X/V$ .

**Equation 6.** Substituting  $X/V$  for  $\tau$  in equation 5 and multiply the numerator and denominator by the width of the pond “Y” yields:

$$ER = MW_{HF} C_{HF} \rho_{air} D_b V Y \pi / 4 X Y (10^9)$$

The following figure is a representation of the dimensional parameters in Equation 6.



The term “XY” is equal to the surface area in  $m^2$  of the pond. After removing the factor “ $\pi/4$ ” and “XY” the remaining term “ $MW_{HF} C_{HF} \rho_{air} D_b V Y / (10^9)$ ” is equal to the mass flow rate through a downwind vertical plane as wide as the pond and with a vertical dimension ( $\Delta Z$ ) equal to the beam width ( $D_b$ ).

**Equation 7.** The actual mass flow rate through the entire vertical plane is more accurately given as:

$$Q = \sum_{i=1}^{i=\infty} MW_{HF} C_{HF_i} \rho_{air} \Delta Z_i V_i Y_i / 10^9$$

Where:

$Q$  = mass flow through vertical plane in  $\mu g$  HF/second

$C_{HF_i}$  = concentration in ppm (of HF) at element “i”.

$V_i$  = wind velocity at element “i”

$\Delta Z_i$  = vertical dimension in meters of element “i” of the infinite vertical plane characterized by  $C_{HF}$  at that height - similar to  $D_b$ .

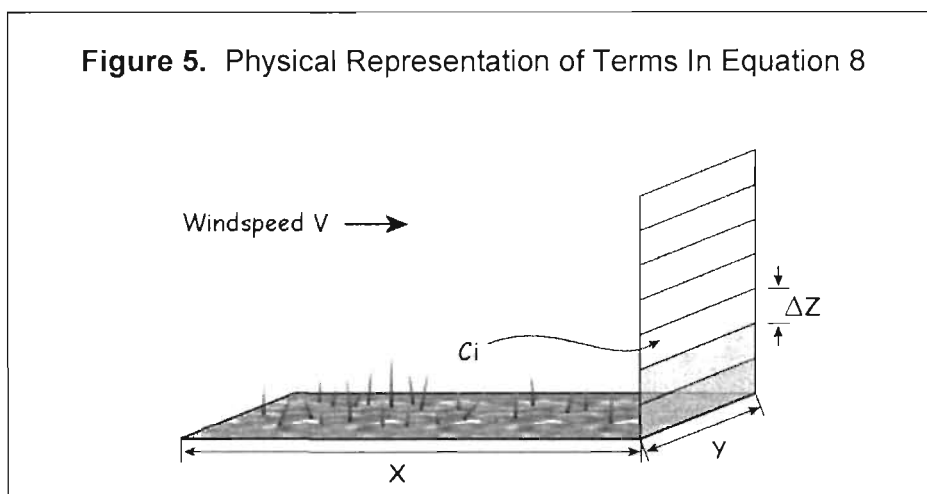
$\Sigma$  - the sum of mass flow rate contributions from all elements where “i” = 1 to infinity.

$Y_i$  – approximate width of element ~ width of pond.

**Equation 8.** Because  $Q$  from the pond must equal  $Q$  through the vertical plane (mass continuity requirement), the emission flux from the pond surface can be estimated as:

$$ER = \sum_{i=1}^{i=\infty} MW_{HF} C_{HFi} \rho_{air} \Delta Z_i V_i Y_i / XY (10^9)$$

The new summation equation “recaptures” the flux above and below the single 0.37-meter element represented by the beam of diameter  $D_b$ . It is sufficient to sum the elements that would fall within a height that reflects a likely “mixing height” or “cap” containing most of the mass emanating from the pond. The mixing height is of much greater magnitude than the diameter of the beam. Ignoring for the moment, variations in wind speed and width of each element, the physical representation of this concept is shown in the figure below:



Radian’s estimate would comprise only one of the elements with a vertical dimension equal to the diameter of the beam. The beam diameter was 0.37 meters compared to the cap, which is estimated on the order of 25 meters. The potential error is roughly two orders of magnitude.

The correct summation methodology for mass flow rate or for flux is given in a number of sources, including the ES&E report discussed above. Additional references for the correct procedure (basically the “plane integrated method” for a box model) are common.<sup>21,22</sup> The method is merely an expression of the equation of continuity of mass flow rate through changing cross sectional areas.

A correction factor of 50 (near the lower end of “two orders of magnitude”) would yield an emission factor between 0.6 and 4.6 based on the range of Radian Analytical Model estimates.

With respect to the Chemical Model, Radian apparently simulated the chemical species as reported in basic pond analyses similar to the list in Table 3 (fluorides) and not as they exist in the pond environment. Thus the Radian Chemical Model failed to account for the most important form of fluoride (fluosilicates) in the pond system. It is doubtful that the model considered equilibria for chukrovite, ralstonite, or alkali fluosilicates given in Table 2, not to mention complicated iron-ammonium phosphates and iron-potassium phosphates.

The fatal flaw in the Chemical Model is enough to discredit it. The details of the model are not readily available so that other features can be reviewed and possible errors detected.

## CONCLUSIONS

Based on the amount of fluoride entering the system, process chemistry considerations, numerous investigations regarding process pond emissions, and corrections of Radian's field effort, it is likely that process pond emissions are greater than 10 TPY of HF. Therefore most phosphoric acid/fertilizer facilities are subject to 40 CFR 63, Subpart AA and BB. This conclusion is supported by all of the published studies including the "minimum" Cross & Ross study previously used by several companies.

## RECOMMENDATIONS

A new FTIR-based study should be conducted (preferably under the auspices of EPA) to definitively measure emissions from process cooling ponds. The instrumentation is now much less expensive and new techniques exist to measure plane-integrated flux using multiple FTIR units and vertical reflector arrangements.

Similarly an effort should be conducted (preferably by EPA) to characterize the fraction of exhaust stack fluoride emissions that are emitted as HF in view of industry claims that are at odds with EPA's findings during promulgation of Subparts AA and BB.

## ACKNOWLEDGEMENTS

The author wishes to acknowledge the insight provided in the numerous papers published by Dr. Ram Hashmonay in the Journal of the AWMA and in the annual conference proceedings. He is perhaps the most prolific author in the estimation of gaseous flux from area sources by remote monitoring techniques.

## DISCLAIMER

The author prepared this paper on his own time. While some of the material was available from the public record, the opinions, conclusions, and recommendations as presented in this paper are those of the author.

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## KEY WORDS

Gypsum Ponds, Phosphoric Acid, Hydrogen Fluoride Emissions, MACT



# Phosphate Processes

## Open-Pit Mining Processes

- Overburden Handling
- Matrix Handling/Transport
- Mine Recirculation Water & Stormwater
- Dragline & Equipment Maintenance
- Reclamation Activities

## Beneficiation Processes

- Washer Section
- Feed Preparation Section
- Flotation Section
- Reagents Storage & Handling
- Wet Rock Drying (No longer used)
- Wet Rock Storage & Shipping
- Waste Sands & Clays Disposal
- Clay Settling Area (CSA) Reclamation
- Air Scrubbers & Control
- Maintenance Activities
  - Equipment Maintenance Wastes
  - Facility Maintenance (turnaround wastes, sandblasting, painting, etc.)

## Chemical Plant Processes

- Phosphate Rock Handling
  - Railcar Unloading Activities
  - Wet Rock Storage Facilities
  - Wet Rock Grinding Circuit
  - Transport & Conveying Processes
- Sulfuric Acid Production
  - Sulfur Handling & Storage (Molten & Prills)
  - Air Drying & Blower Control
  - Sulfur Burning, Conversion & Absorption
  - Air Scrubbers and Mist Control
  - Sulfuric Acid Cooling & Storage
  - Truck & Railcar Loading Activities
  - Heat Recovery & Steam Production
  - Demineralized Water Production
  - Cogeneration Process
- Phosphoric Acid Production
  - Reaction & Filtration
  - Defluorination
  - Concentration
  - Air Scrubbers & Control
  - Phosphogypsum Transport & Storage
  - Truck & Railcar Loading Activities
  - Process Water Handling & Cooling
- Hydrofluosilicic Acid Manufacturing
  - Condensation Process
  - Transport & Storage
  - Truck & Railcar Loading Activities
- Fertilizer Manufacturing
  - MAP (Monoammonium Phosphate)
    - Reaction, Granulation, Drying, Classification & Storage
  - DAP (Diammonium Phosphate)
    - Reaction, Granulation, Drying, Classification & Storage

- GTSP (Granular Triple Superphosphate)
  - Reaction, Granulation, Drying, Classification & Storage
- ROP (Run-of-Pile Triple Superphosphate)
  - Reaction, Storage, & Curing
- Truck & Railcar Loading Activities
- Air Scrubbers & Control
- Ammonia Storage & Handling
- Animal Feed Phosphates Manufacturing
  - Reagents Storage & Handling
  - Feed Preparation
  - Phosphate Rock Defluorination
  - HF Recovery & Storage
  - Phosphoric Acid Defluorination
  - Calcium Enriched Phosphates
  - Air Scrubbers & Control
  - Classification, Transport & Storage
  - Truck & Railcar Loading Activities
- Uranium Recovery (No Active Production in Florida)
  - Closure of Sites
- Elemental Phosphorous (No Active Production in Florida)
  - Closed Sites
- Lab Operations & Wastes Handling
- Maintenance Activities
  - Equipment Maintenance Wastes
  - Facility Maintenance (turnaround wastes, tank inspection, lining & cleanout wastes, sandblasting, painting)

Product Shipping & Ammonia Terminals

- Truck & Railcar Unloading Activities
- Product Storage Facilities
- Phosphate Rock Drying
- Air Scrubbers & Control
- Material Transport & Ship Loading Operations
- Ammonia Unloading & Storage Activities
- Ammonia Heating, Pumping & Pipeline Operations
- Non-Process Wastewater & Stormwater Storage/Treatment/Disposal
- Maintenance & Cleanup Activities

Environmental Concerns

- Mining Facilities
  - Maintenance Wastes for Draglines & Other Heavy Equipment
  - Matrix Slurry & Mine Water Return Pipeline Leaks
  - Reclamation Dams Construction & Integrity
  - Stormwater Treatment & Disposal
- Beneficiation Plants
  - Fate of Reagents
    - Ammonia was added for pH control out of cyclones
    - Fatty Acid is added to coat phosphate particles
    - Diesel Fuel is added to form bubbles and help float phosphates
    - Sulfuric Acid ( $H_2SO_4$ ) strips fatty acid off
    - Amines are added to get sand particles to float (phosphates will sink)
  - Maintenance Wastes (Solid & Hazardous)
  - Sand Tailings Transport & Disposal
  - Waste Clay Transport & Disposal
  - Stormwater & Mine Recirculation Water Storage/Disposal
  - Rock Dryers (None active, only a couple of closed ones)

- Spent scrubber packing & wastewater
- Air Scrubbers & Control
- CSA Dams Construction & Integrity
- Chemical Plants
  - Maintenance Wastes
    - Pipe Scale Waste Handling
    - Solid Waste Disposal
    - Hazardous Waste Storage & Handling
  - Air Emissions & Control
    - Ammonia Releases
    - SO<sub>2</sub> Releases
    - Sulfuric Acid Mist Emissions
    - Fluoride Emissions
    - Particulate Emissions
  - Phosphogypsum Stacks & Process Water Cooling Ponds
  - Process Water, Non-Process Water, & Stormwater Storage/Treatment/Disposal
    - Wastewater Quality, Wastewater Quantity & Nutrients
  - Phosphogypsum Stack System Closure Activities
- Product Shipping & Ammonia Terminals
  - Air Emissions & Control
    - Ammonia Releases
  - Maintenance Waste Handling
  - Wastewater & Stormwater Quality, Storage, Treatment & Disposal