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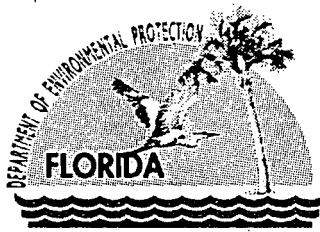
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David B. Struhs
Secretary

December 23, 2002

CERTIFIED MAIL – RETURN RECEIPT REQUESTED

Mr. Bruce D. DeGrove
Director, Regulatory Affairs
The Florida Phosphate Council
1435 East Piedmont Drive, Suite 211
Tallahassee, FL 32308

Re: Issues From 1999 Radian Report. Measurement and Modeling
HF Emissions from Phosphoric Acid Production Facilities

Dear Mr. DeGrove:

Thank you for your response dated November 1 to the six issues identified in our communication to you dated September 12, 2002. We appreciated the opportunity to meet with you, your members, The Fertilizer Institute, and Dr. Jeffrey LaCosse of Spectral Insights on November 20th.

As you know, the Division of Air Resources Management (DARM) retained Dr. Arthur Fricke, Professor Emeritus, of the University of Florida's Chemical Engineering Department as an objective, independent consultant to provide the best technical opinion on the matter. He evaluated the Radian Report that was used as a basis for the Industry's estimates of hydrogen fluoride (HF) emissions from the ponds in question. Attached for your review and consideration is Dr. Fricke's evaluation of the Radian analytical and chemical models. Dr. Fricke's calculations reveal problems with both of Radian's models as described below.

First, Dr. Fricke concludes that the basis used by Radian for estimating the HF emissions from the FTIR data in their "analytical model" is grossly in error. His conclusion, based on use of the HF concentrations measured by Radian, is that the emission factor is actually in the range of 0.5 to 2 pounds of hydrogen fluoride per acre per day (lb HF/acre-day). Second, and as an alternative to Radian's chemical model, Dr. Fricke performed calculations based on basic principles of mass transport phenomena. Emission factors calculated by the latter techniques are even greater. Dr. Fricke's calculations for both the analytical and chemical models reveal emissions factor values of roughly two orders of magnitude higher than the emission factors in the Radian Report.

We need to move ahead with this issue so a quick review of the report is appreciated. If the plants are in a position to discuss how this data could be used in resolving issues with the EPA, we can work with you in the permitting process to accomplish those goals.

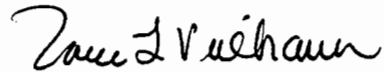
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Mr. Bruce DeGrove
December 23, 2002
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Please contact me as soon as possible to discuss how the individual permittees would like to proceed with this matter. Feel free to let them know they may also contact me directly.

Sincerely,



Trina L. Vielhauer, Chief
Bureau of Air Regulation

Enclosure

TLV/aal

Cc: Gerry Kissell, DEP SWD
Chris Kirts, DEP NED
Jerry Campbell, EPCHC

Arthur L. Fricke
1502 NW 110th Terrace
Gainesville, FL 32606
December 14, 2002

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Florida Department of Environmental Protection
Division of Air Resource Management
2600 Blair Stone Road, Mail Stop 5500
Tallahassee, FL 32399
(850)-921-9533
Alvaro.Linero@dep.state.fl.us

RE: Evaluation of the Radian Report on "Measurement and Modeling of HF Emissions from Phosphoric Acid Production Facilities"

Dear Mr. Linero:

As requested, I have made as complete a critical review as possible of the Radian report on HF emissions, including an estimate of HF emissions by vertical integration of gaseous HF flow from the ponds studied using the data reported by Radian, as requested by Mr. John Reynolds of the Division of Air Resource Management of the Florida Department of Environmental Regulation.

The main documents that I reviewed critically are:

1. "Measurement and Modeling of HF Emissions from Phosphoric Acid Production Facilities: Final Report", Project No. 197-002, Radian Corporation, 9/22/93.
2. "FDEP Issues Review, Memo from J. P. LaCosse, Spectral Insights, LLC to W. Hertz, TFI, 11/1/02.

In conducting this review, I reviewed other pertinent sources and used reference sources for comparison and for correlations and data needed to conduct my critical review.

Overall, I found these documents to be difficult to review. Basically, the FTIR measurements appear to have been very well conducted and the methods used are reported in (1) in great detail. Unfortunately, the remainder of the reporting and reporting of the modeling done by Radian are very poor and incomplete.

There are a number of typographical errors and/or mistakes in the text of (1), the documentation needed to quantitatively review the "analytical and "chemical" models is incomplete (particularly for the "chemical" model), and there are conflicts or uncertainties in certain quantities. As examples, the measuring beam diameter is stated to be 37 cm in (1) and 40.3 cm in (2); the measurements are stated to be across a line perpendicular to the wind direction in (1) while there is a reported nearly 60° difference in wind direction reported in (1) for data taken during two tests at Cargill; the measuring height is reported as 3 to 4m above the pond surface (this makes a difference in analyzing the results); and the height for measurement of the wind speed is not specifically stated (I presume that this was measured at 3 to 4m).

The basis used by Radian for estimating the HF emissions from the FTIR data in their "analytical" model is grossly in error. The model assumes that all HF emissions from the pond pass through a 0.37m high by 100m long double path measuring beam. I am certain of this, because the

data for HF concentrations and for the calculated “analytical” model HF emission rates given in Tables 3-6 and 3-7 of (1) are consistent with this interpretation. This is a physical impossibility. All of the air containing HF emissions from passing over the pond cannot possibly be compressed and forced to flow through a 0.37m slit 3 to 4m above the pond as required by the Radian “analytical” model. In addition, the equations cited in (1) and (2) for emissions (as best as I can tell) calculate the air flow through the measuring beams based on flow through two cylinders 0.37m in diameter rather than the proper rectangle of 0.37m high by 0.74m long. In my calculations, I have used the concentration reported as an average concentration for air flow through a 0.37m high by 100m wide slit (which are the correct dimensions for air flow through the measuring beam).

I have performed integrations in the vertical direction of HF emissions for the four cases studied by Radian. As the bases for these calculations, I:

1. Accepted Radian HF concentration measurements given Tables 3-6 and 3-7 as correct.
2. Assumed that air flow was perpendicular to the measuring beam (this is not always true, as can be seen from the wind directions given in Table 3-7).
3. Assumed the average wind speeds stated were meteorological maximum wind speeds, rather than the wind speed at 3 to 4m. This assumption results in considerably lower wind speed at 3 to 4m above the pond than the actual measurement stated in the Radian report, if indeed the wind speed was measured at 3 to 4m above the pond by Radian.
4. Assumed the HF concentration in air was measured at 3m and forced the concentration profiles used in my calculations to agree with the reported concentrations at 3m.
5. Assumed that the HF equilibrium vapor pressures reported in Tables 3-3 and 3-5 of the Radian report were correct, although they are at the low end of values measured or estimated in other studies. Since the vapor pressure relation is quite uncertain, it seemed prudent to accept the Radian values for conservative calculations.
6. Used correlations given in Fluid Mechanics, 3rd Ed., F.M. White, McGraw-Hill(1994) and in Momentum, Heat, and Mass Transfer 3rd Ed., C. O. Bennett & J. E. Myers, McGraw-Hill(1982) to estimate the boundary layer thickness (δ) for the cases as being closest to more sophisticated meteorological correlations, even those these correlations predict lower boundary layers than the concentration boundary layer thickness predicted by the more sophisticated meteorological correlations. I used the Blasius relation to estimate the wind speed vs. vertical distance as equal to $(\text{height}/\delta)^{(1/7)}$ x average wind speed, where the reported wind speed was taken as the maximum wind speed rather than the wind speed at 3m. The correlation given by White is $(\delta/\text{distance})=0.16/(\text{Re}_x)^{(1/7)}$ and the correlation given by Bennett & Myers is $(\delta/\text{distance})=0.376/(\text{Re}_x)^{0.2}$.
7. Assumed that the concentration profile in the boundary layer was the same as the air speed profile up to a distance such that the concentration at 3m agreed with Radian’s reported value, and assumed that the concentration profile was linear from this distance to the top of the boundary layer where the concentration was set equal to zero. The concentration at the surface was set equal to the equilibrium vapor concentration reported by Radian for each case.
8. Integrated vertically in intervals of 0.37m, since this was the FTIR beam width used by Radian. Smaller intervals would have required fitting the calculated velocity and concentration curves as a function of vertical distance. This was not deemed advisable, since the concentration measured by FTIR was an average over 0.37m at a somewhat uncertain

height and there are no concentration profile data. I have only measured a value vs. height (a somewhat uncertain height), a value calculated from theory for the surface, and an assumed concentration of zero at the boundary height..

These assumptions should lead to a conservative estimate of HF emissions, even though the exact concentration profiles for the four cases are not known. The calculations I have made ignore dispersion of HF into the air parallel to the long dimension of the ponds, give conservative estimates of wind speeds vs. height, and most probably do not adequately represent mixing in the turbulent boundary layer. The purpose of the calculations was to make more realistic, but conservative, estimates of HF emissions from the ponds based on the Radian measurements of HF concentrations in air above the ponds. Integration was performed in 0.37m increments of height with the wind speed and HF concentration set at the average values for each increment and the total HF flow for the pond surface determined as the sum of HF flow calculated for each increment.

The results of the calculations for the four cases in terms of micro-gms/m²-sec and lbs/acre-day, along with necessary data on the ponds(wind speed, contact distance, temperature, concentration at 3m) and Radian results for the “analytical” model for the same four cases, as given or converted from values in Tables 3-6 and 3-7 of (1) are given in the following Table. A disk copy of the excel spreadsheets used in performing the necessary calculations can be made available upon request.

Integration and Radian “Analytical” Model Results for HF Emission Rates for the Four Cases Reported by Radian in (1)

Case	Wind Speed, m/sec	Radian Emission Rate, micro-gm/m ² -sec	Radian Emission Rate, lb/acre-day	Integrated Emission Rate, micro-gm/m ² -sec	Integrated Emission Rate, lb/acre-day	HF Conc, @ 3m ppb(v)	Temp, F	Contact Distance, m
IMC (1)	3.4	0.13	0.1003	1.96-1.89	1.51-1.46	62.0	80	400
IMC (2)	3.1	0.093	0.07253	2.67-2.71	2.06-2.09	47.7	90	400
Cargill(3)	1.2	0.0033	0.002544	0.667-0.805	0.513-0.621	11.1	80	1000
Cargill(4)	4.6	0.041	0.03161	1.32-1.23	1.02-0.948	45.8	90	1300

There are two values reported for the integrated emission rate for each case. The first is that obtained by using the correlation given in Bennett & Myers and the second is that obtained using the correlation given in White. The emission rates calculated by vertical integration are much higher(more than an order of magnitude higher) than those reported by Radian using their “analytical” model. While these emission rates calculated by vertical integration are only approximate, I believe that they are much nearer the truth than the values for emission rates reported by Radian; if anything, the integrated emission results are very likely conservative (too low) for the

reasons given in the list of bases for calculation that precedes the table. The emission rates calculated by vertical integration using the Radian data are in closer agreement with earlier reported studies, and (except for the value for Cargill(4)) appear to be in closer agreement with each other. It is possible that the lower than expected value for Cargill (4) may be partly due to wind direction. In any case, it seems clear that the emission rates reported by Radian are incorrect.

The “chemical” model of Radian is even harder to evaluate, because the information given is very incomplete, and there are some serious questions that arise. It is stated in the Radian report that the liquid is treated as a batch biological reactor, and zero order kinetics are used for the batch reaction with the reaction constant given as the overall mass transfer coefficient. This is patently incorrect; the ponds are flow systems, not batch systems.

Secondly, the vapor pressure of HF vs. temperature (and also, implicitly, concentration) is calculated using a thermodynamically based computer program(ACAPP) that is not available to me. It is stated in (1) that inputs for the program number 12 for the IMC pond and 8 for the Cargill pond, and these inputs are basically elemental analyses results and pH. When one considers the number of reactions involved (not all of which may be in equilibrium at all times), the interactions that can occur between ionic pairs and beyond, and the presence of three phases (liquid, solid, gas), it stretches belief to the limit to accept that the activity of a particular component (especially one that is not present in the major amount) can be calculated accurately as would be necessary to accurately estimate the vapor pressure of that component in the solution. It might also be pointed out that equilibrium may not (indeed, probably does not) exist at all times in the pond. There is not enough information given to warrant acceptance of these values with certainty. Therefore, the vapor pressures calculated are questionable, and this is stated in the Radian report to be a basis for the chemical model. Indeed, Dr. LaCosse implicitly admits to this uncertainty in (2). There does not appear to be any reliable vapor pressure data for HF for pond liquids. However, it does appear that Radian’s calculated vapor pressures are at the lower end of the expected range.

Calculated vapor pressures are reported vs. temperature, but not vs. HF concentration. Since the two-film theory requires the slope of the partial pressure vs. liquid concentration curve, this required value (the slope) is not reported nor can it be calculated from the values reported. With only one value of vapor pressure vs. concentration, one must assume that a straight line passing through this point and the origin defines the required slope, m . That is, Henry’s law must be assumed to apply. Dr. LaCosse claims that this is not so, but I cannot understand from the response (2) what was used as an alternative to define the slope.

Reporting on individual mass transfer coefficients in (1) is incomplete; i.e., non-existent. Not a single value is reported nor is one sample calculation cited. A list of correlations is given in Appendix A of (1), but it is not stated which was used. Most are not appropriate. Those listed by Springer et al are referenced to the mass transfer of ether in water and I believe that they are intended for use for organic compounds in water. In addition, two are limited to liquids with a depth to length ratio less than 51.2. Even for a 400m long pond, this would require a liquid depth of at least 25.5 ft. Those listed as by Mackay and Yuan are the most appropriate, but it is not stated in the Radian report if these were used. The applicability of the one listed for the gas phase is questionable, because it contains an “equivalent diameter” term. As the length to width ratio of the pond becomes larger, this correlation most likely becomes less applicable. While this correlation may be applicable, its use by Radian is only implied by the fact that it is the only one listed for the gas phase. No sample

calculations are given for these coefficients nor are values reported for the four trial cases.

Graphs are presented in (1) reportedly representing computer calculated results of HF emissions as a function of wind speed with temperature as a parameter for the IMC and Cargill ponds, but no bases (specific correlations, example values, calculating equations, or codes) are given for these. Without such documentation, it is impossible to evaluate the validity of these results presented in graphical form in (1). However, the results are highly suspect for the reasons given above and for the additional reason that the use of the two film theory upon which these calculations are supposedly based is questionable for use for extended contact times between phases (as exists in the case of these ponds). The results of Radian's "chemical" model should be rejected as undocumented and basically incorrect for the reasons given above.

As an alternative to Radian's "chemical" model (the only thing that I can do as a check) for these four cases would be to consider diffusion through the gas laminar layer above the pond and to consider mass transfer of the HF through the gas phase using a mass transfer coefficient correlation cited by Radian and a correlation cited by Sherwood, Pigford, and Reid for mass transfer from a flat liquid surface into a gas in turbulent flow. For a driving force, I used the difference between the liquid vapor pressure and the HF concentration at 3m in the flowing air. This is probably not truly correct, since I am dealing with only one transfer coefficient and I do not know that the gas phase transfer is controlling. However, it is the best that I can do with the data given. Diffusivity of HF in air can be quite accurately estimated for dilute systems, since there are really only three components in the gas phase (air, water vapor, and HF). The laminar boundary layer thickness can be reasonably estimated using correlations for flow over flat surfaces. The total pressure and temperature are cited, the wind speed at 3-4m is cited, and the dimensions of the ponds as a basis of calculation are given. The concentration of HF in the gas phase at the elevation of the stagnant laminar film can be estimated from data at 3m and from the wind speed. On these bases, the molar flux rate of HF from the pond can be estimated from the diffusion rate of HF from the pond surface through a stagnant film or from the mass transfer rate calculated using the mass transfer rates for the gas phase. This is at least a rational approach for estimating HF emission rates from the ponds as a check on Radian's "chemical" model approach.

I have performed these calculations. The results, along with Radian's "chemical" model results cited in their report are given in the following table.

ESTIMATED EMISSION RATES (lb/acre-day)

**BASED ON MASS TRANSFER IN THE GAS PHASE WITH COMPARISON TO
RADIANS "CHEMICAL" MODEL RESULTS-(lb/acre-day)**

Method	Radian Chemical Model	Diffusion through a gas film	Mass Transfer using Radian's cited Correlation	Mass transfer using Sherwood et al cited correlation
IMC(1)	0.0162	3.74	3.91	1.82
IMC(2)	0.0200	4.76	5.05	2.23
Cargill(1)	0.0067	0.998	1.37	0.581
Cargill(2)	0.0316	5.24	5.74	2.31

These estimates are very approximate, but clearly show that Radian's "chemical" model results are highly questionable. It is worth noting that the trends in emission rates for all three calculation bases that I used in making my estimates are the same. Also note that the results for diffusion through a laminar film and the results for mass transfer through the gas using the correlation cited by Radian are in reasonable agreement. The emission rates estimated for mass transfer through the gas made by using the correlation cited by Sherwood, Pigford, and Reid are less than half of the emission rates estimated by the other two calculations, however. In either case, the predicted emission rates in my estimates are about two orders of magnitude greater than those reported by Radian for their "chemical" model.

The estimates I have made by using the chemical analyses and wind speed data of Radian for calculating emission rates by vertical integration of the estimated velocity and concentration profiles and the estimates that I have made on the basis of mass transfer through the gas phase or by considering diffusion of HF through a laminar film above the liquid surface are in rough agreement. Calculated emission values all lie between about 0.6 and 5.74 lb/acre-day for the four cases. For any individual case, agreement between the integrated value and the mass transfer value using the correlation cited by Sherwood, et al is quite good, and these are more than two orders of magnitude greater than those reported by Radian in (1). Moreover, the estimated rates of 0.6 to 5.74 lb/acre-day are in reasonable agreement with values reported from earlier work.

It should be noted that exact determination of emissions in such small amounts from such a large physical source is an extremely difficult problem. Furthermore, the data collection methods required are complex and expensive. Any study intended for such a purpose should be thoroughly planned all the way through the necessary calculation procedures before beginning the physical

work. Ordinarily, these would be thoroughly reviewed by those experienced in each phase of the necessary work, estimates of expected ranges of uncertainty made, and a preliminary test (possibly a gamed review) would be conducted. I really question whether this was done for this study as performed by Radian.

While the chemical analysis methods used by Radian were excellent, the experimental planning with respect to the data needed and evaluation of the data were apparently not adequate to permit them to accomplish the goal of accurately measuring HF emissions from these ponds. The basic report (1) is very deficient in documenting details necessary to support their calculated results. In my opinion, Radian's results cannot be used to define emissions from these ponds nor for accurate estimates of emissions from other similar ponds.

The results of calculations that I have made are approximate, but undoubtedly conservative estimates that are undoubtedly much nearer the truth than the results reported by Radian in (1). There are just too many uncertainties in estimating the velocity and concentration profiles as well as problems with the geometry of the ponds where these measurements were taken and the problem of adequately compensating for horizontal dispersion parallel to the wind direction to make estimates of HF emissions for these four cases with the desired engineering accuracy of about +/- 25-30% for mass transfer estimates. The data given in the Radian report is not adequate for such accuracy. What can be stated with certainty, however, is that the results of calculations that I have made, particularly from vertical integration of data reported by Radian, are conservative estimates of HF emissions for these four cases. That is, emissions must range from at least 0.67 to 1.51 lbs/acre-day (0.122 to 0.275 tons/acre-yr) for these four cases rather than the 0.0025 to 0.1 lbs/acre-day (4.6×10^{-4} to 0.018 tons/acre-yr) reported by Radian for their "Analytical" model. Radian's estimates of emission rates have to be low by more than an order of magnitude (more than 1000%).

Respectfully,



Arthur L. Fricke

cc: Mr. John Reynolds

Florida Department of Environmental Regulation

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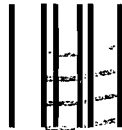
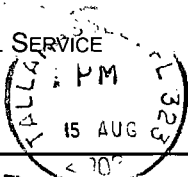
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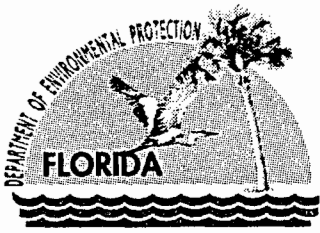
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David B. Struhs
Secretary

August 12, 2002

CERTIFIED MAIL – RETURN RECEIPT REQUESTED

Mr. Bruce D. DeGrove
Director, Regulatory Affairs
The Florida Phosphate Council
1435 East Piedmont Drive, Suite 211
Tallahassee, FL 32308

Re: Issues From 1999 Radian Report. Measurement and Modeling
HF Emissions from Phosphoric Acid Production Facilities

Dear ^{Bruce}Mr. DeGrove:

Attached is a preliminary listing of the most significant issues that we question from the Radian Report regarding hydrogen fluoride (HF) emissions from gypsum/cooling ponds. These issues suggest that the emission estimates given in the report are considerably less than actual emissions from the ponds. Perhaps these are the ones that need to be focused on in future discussions.

Our good faith effort of supplying you with our opinions first may help stimulate the discussion so we can arrive at a speedy conclusion of this issue.

We are awaiting data related to stack emission tests conducted by the industry to determine the relative breakdown of fluoride between gaseous and particulate components.

I look forward to discussions with you or member companies at an early date. In the meantime, if you have any questions regarding this matter, please contact Ms. Cindy Phillips at 850/921-9534 or Al Linero at 850/921-9523.

Sincerely,

Howard L. Rhodes, Director
Division of Air Resources
Management

Enclosure

HLR/aal

Cc: Jerry Kissell, DEP SWD
Chris Kirts, DEP NED
Jerry Campbell, EPCHC

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EVALUATION OF RADIAN REPORT FOR ESTIMATION OF HYDROGEN FLUORIDE EMISSIONS FROM GYPSUM/COOLING PONDS.¹

Radian's Summary: (partially paraphrased and simplified by Department)

Radian Corporation was contracted by The Fertilizer Institute, Inc. (TFI) to determine if HF and SiF₄ are present in the emissions from cooling ponds at phosphoric acid production facilities and to assess methods for evaluating emission rates from the ponds. Fourier transform infrared (FTIR) spectroscopy was used to perform a series of measurements at two institute member phosphoric acid manufacturing facilities: IMC Fertilizer, Inc. located in Mulberry, Florida and Cargill Fertilizer, Inc. facility located in Riverview, Florida.

HF and SiF₄ concentrations were measured using an FTIR open path spectrometer coupled with a meteorological sensing station. The surface impoundment measured at each facility was a large cooling pond which was suspected to be a source of emissions. 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.

HF was detected at all times at both sites. The open-path FTIR detection limit for HF was 2-3 ppb for a single 5 minute measurement while that of SiF₄ was 0.3 ppb. At IMC, SiF₄ was detected only during a short period of time. Following is a summary table of measurement results.

Table 1. Field Measurement Summary (in ppb) Summer/Winter Conditions

Site	Max. SiF ₄ (ppb)	Mean SiF ₄ (ppb)	Min SiF ₄ (ppb)	Max HF (ppb)	Mean HF (ppb)	Min HF (ppb)
IMC (S)	3	0.5	0	100	57.7	22
Cargill (S)	0	0	0	81	23.2	2
Cargill (W)	(a)	(a)	(a)	35	6.7	0
Cargill (W,b)	0	0	0	28	15.6	7

(a) Measurement not made

(b) Measurement above pond surface

(s) Summer, 1993

(w) Winter, 1994

FTIR open-path detection limits (5 minute average): HF = ~1ppb, SiF₄ = ~0.5 ppb

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 pond chemical modeling/mass-transport model.

The following table gives the results for the chemical and analytical modeling techniques for HF. Both models are still in the developmental stage, so the results should not be taken as absolute. However, the agreement between the two models is quite good despite their stage of development. (Department disagrees with this statement)

¹ Lacrosse, J.P., Ph.D. et al., Radian Corporation. Measurement and Modeling of HF Emissions from Phosphoric Acid Production Facilities. Prepared for The Fertilizer Institute. 1993. Amended April 1999.

Table 2. Preliminary Model Results – Site Averages (Hydrogen Fluoride Only)

Site	Time-Weighted Chemical Model Emission Rate (lb/acre-day)	Time-Weighted Analytical Model Emission Rate (lb/acre-day)
IMC (S)	0.018	0.092
Cargill (S)	0.013	0.012
Cargill (W)	0.015	0.012

(s) Summer

(w) Winter

(Note: Radian used the Chemical Model Results to Estimate ~ 2 tons per year of HF from pond)

Issue 1 – Derivation of Emission Rate Equation in the Analytical Model

Radian developed an emission rate equation to use in conjunction with the concentrations and wind speed measured over or adjacent to the pond system. The equation is as follows (page 20):

$$ER = MW_s \cdot C_s \cdot \rho_{air} \cdot D_b / 4 \cdot \tau$$

Where:

ER = emission rate in micrograms/m²/second

C_s = concentration of species in ppbv

ρ_{air} = number density of air in moles/m³

D_b = diameter of optical beam in m

τ = average time for air parcel to travel over pond in seconds (fetch)

MW_s = molecular weight of species s in grams/mole

Derivation of the equation is given in Appendix B of the report. Of particular interest to the Department is the factor “τ”. If this is on a large timescale (hundreds of seconds to travel over the pond), then the emission rate will be very low. If the factor is on a small time scale (fractions of a second to cross the beam) the emission rate will be much higher. Our own efforts to reproduce the derivation using the two equations described in Appendix B lead to a similar final equation but without a factor of 4 in the denominator. This alone could increase estimates of emissions by a factor of 4.

Issue 2 – Henry’s Law Constant and Mass Transfer Coefficients used in the Chemical Model

The “Chemical Model” emission rate depends on an attempt by Radian to calculate the vapor pressure of HF, its liquid and gas-phase mass transfer coefficients, and the effect of wind speed on mass transfer.

The key component is the hazardous air pollutant (HAP), hydrogen fluoride, which exists in the pond where it is theorized to exert its vapor pressure with some tendency to leave the solution. In *dilute solutions*, vapor pressure of a soluble gas behaves in accordance with “Henry’s Law.” Using a “common expression” of Henry’s Law, the relation as applied to the species HF is:

$$p_{HF} = k_{Hinv} [HF]$$

Where: p_{HF} is the partial pressure of HF in the gas phase in atmospheres (atm)

[HF] is the concentration of HF in the liquid phase in $M = \text{mol}_{\text{aq}}/\text{L}_{\text{aq}} = \text{mol}_{\text{aq}}/\text{dm}^3_{\text{aq}}$

“ k_{Hinv} ” is Henry’s Law Constant (in this case for HF) $\text{atm}/M = \text{atm}\cdot\text{dm}^3/\text{mol}$

It is not known exactly how Radian derived the vapor pressure for HF in a pond water system. Radian used its “Aqueous Chemical And Physical Properties Program” (ACAPP). The following table lists the pond water analysis used as input parameters for ACAPP modeling of the IMC and Cargill ponds:

Table 3. Input ACAPP Parameters for the IMC and Cargill Facilities

<u>Component</u>	<u>Concentration at IMC (mg/L)</u>	<u>Concentration at Cargill (mg/L)</u>
Na	2,450	2,790
K	390	416
Al	320	34
SO ₄	8,500	4,800
SiO ₂	6100	1,840
F	11,200	9,660
CaO	2,600	
P ₂ O ₅	23,600	22,980
Fe	230	
NH ₄	2,200	
Mg	420	
H ⁺	pH = 1.26	pH = 1.80

It appears that “F” was assumed to be fluoride ion, including all fluoride regardless of form, and not just HF. Therefore, Radian’s Henry’s Law Constant cannot be the real constant for HF. According to Radian, these parameters were used as inputs for several ACAPP simulations between 80 and 100 °F. The resulting partial pressures were used by Radian to estimate the Henry’s Law Constants listed below.

Table 4. Computed Vapor Pressures for IMC and Cargill Facilities (above pond surface)

Facility	IMC		Cargill	
	Vapor Pressure (ppbv)	Henry’s Constant (atm·m ³ /mol)	Vapor Pressure (ppbv)	Henry’s Constant (atm·m ³ /mol)
80	781	1.22x10 ⁻⁹	718	1.41x10 ⁻⁹
90	1065	1.81x10 ⁻⁹	970	1.91x10 ⁻⁹
95	1239	2.10x10 ⁻⁹	1129	2.22x10 ⁻⁹
100	1441	2.44x10 ⁻⁹	1314	2.58x10 ⁻⁹
110	1949	3.31x10 ⁻⁹	1780	3.50x10 ⁻⁹

Because most of the aqueous F in the pond exists as SiF_6^{-2} _{aq}, and other complex ions, there is no way that Henry's Law can describe this system. If the fluoride measured in the liquid phase is not the same species as emitted in the gas phase, it is fruitless to talk about Henry's Law Constant per se.

It is also known that the linearity in the relationship (at least on log-log paper) between total pondwater fluoride and HF vapor pressure falls apart at values somewhat less than fluoride values in pondwater (towards the more dilute values where Henry's Constant is even worth discussing).

Radian did not show any calculations using the selected mass transfer coefficients, stating that these were empirically derived for non-aerated surface impoundments. Consequently, a thorough review of their chemical modeling and mass transfer calculations is not yet possible. Calculations using basic correlations for evaporation from liquid bodies under stagnant air condition, suggest minimum emissions from one to two orders of magnitude greater than the emissions factors developed from the Chemical Model. Further it is noted that the empirical coefficients Radian used were developed for organic solutes only. Since HF is not an organic compound, its empirical coefficients may be significantly different.

In any event we know that the overall mass transfer coefficient calculated by Radian should be higher (and thus emissions will be higher) because Radian's Henry's Law Constant is understated.

Issue 3 – Emission Factor Used by Industry is Very Low Compared to other Published References

Radian developed different factors based on two different models. Factors using the Analytical Model (in conjunction with field measurements), ranged from 0.012 pounds per acre per day (lb/acre-day) for the Cargill Plant to 0.092 lb/acre-day for the IMC Plant. It is noted that no plant used the result of the Analytical Model from IMC as the estimator for its own plant (including IMC).

Factors using the Chemical Model (requiring no FTIR field effort by Radian) ranged from 0.013 to 0.018 lb/acre-day.

The Department reviewed ten other references. Estimates given in or inferred from these references range from 0.16 to 10 lb/acre-day. By comparison, the value used by PCS to estimate HF emissions from its ponds is 0.016 lb/acre-day.

The other values from the literature are 10 to 625 times greater than the estimate used by PCS. Even the lowest of those estimates would make the plants major sources of HAPs due solely to emissions from the ponds.

Issue 4 – HF Emissions seem Unrealistically Low versus the Amount of Fluorides Processed

A typical "large" phosphoric acid plant making 4000 tons per day of P_2O_5 will process approximately 150,000 tons per year (TPY) of fluorides contained in the incoming phosphate rock. Almost all fluoride that does not remain in the concentrated phosphoric acid will go to the pond system as solids or as aqueous species.

According to Radian's report, (Page 79) HF emissions from the pond system of a facility similar to that described, are about 2 tons per year. The companies believe that emissions from the stack are also very low and that the sum of HF from stacks and ponds is less than 10 TPY.

Much of the fluoride will at some time exist in the gaseous phase during reaction and concentration, or is exposed to high temperature (including gypsum drying surfaces), or is exposed to a very large surface area. That means that somehow the processes occurring in the plant and pond would have to be so efficient at keeping fluoride in solid form (chukrovite, fluorspar, fluosilicates, particulate emissions, etc.) or recovered or locked up in the liquid phase (e.g. fluosilicic acid), that not even 10 tons per year escape as HF from the stacks and ponds combined.

Ten tons is less than 0.01 percent of the fluoride processed in one year (99.993% efficiency of conversion to species other than gaseous HF). This is doubtful given the tonnage of fluoride that can exist as HF in the gaseous phase within the process prior to removal by fluosilicic acid recovery (if employed) and pondwater scrubbing.

Issue 5 – HF Concentration Measurements Are Not Representative

It is noteworthy that HF concentrations were measured during a very few days at Cargill and IMC during the summer of 1993 and at Cargill during the winter of 1994. The entire “summer” effort at Cargill was June 4 through June 6, 1993. That is hardly enough time to optimize positioning of equipment, duplicate data, correlate sampling data to meteorological data, etc.

Sampling may not have included the “hot parts” of the pond systems. The first “hot area” is the shallow settling zone where gypsum settles out and ultimately is “mined” and stacked. See Issue 6 for discussion of SF Phosphates where a hot spot was shown to be this area.

The second “hot area” would be where process and cooling waters from sources such as the barometric condensers and scrubbers enter the pond. Such water is laden with a great deal of the HF and SiF_4 evolved during the concentration of the weak acid. Conversion to H_2SiF_6 is not 100 percent. It is not difficult to imagine that this relatively hotter water has a tendency to re-evolve some of the two constituents to a larger extent than the bulk of the pond water.

Radian’s measurements occurred approximately 3 to 4 meters above the surface (1 meter during winter sampling). Radian did not conduct sampling in the vertical direction to determine the variation of concentration, maximum concentration versus height, and possibly a “cap” or “ceiling.”

Another matter of importance is representativeness with respect to wind direction. If the point is to estimate average emissions rather than just average concentration, then it is necessary to always measure downwind from the pond system or over the pond. It appears that some measurements contributing to mean concentration and emissions were not downwind of the source. This means there were concentrations (and thus emissions) downwind that were not represented in the overall estimations of emission factors.

Issue 6 – A Smaller Fertilizer Facility already concluded it is a Major Source of HF

SF Phosphates of Rock Springs, Wyoming is an affiliate of Farmland Hydro in Florida. The complex includes one of the newest phosphate plants in the country. The company is required to continuously monitor ambient fluoride concentrations and report average ambient concentrations based on 12 and 24 hour intervals as well as 7 and 30-day rolling average intervals. The Rock Springs site did not meet the compliance standards in 1994, 1995, and 1996.²

The matter was so serious that the company considered using fluosilicic acid recovered from the process to acidulate some of the phosphate rock in an effort to permanently “fix” the volatile fluorides as marketable CaF_2 .

Subsequent FTIR measurements identified the areas of greatest fluoride emissions emanating from the pond system and the breakdown between HF and SiF_4 . Previous to 1998, the company reported fugitive HF emissions to EPA of less than 10 tons per year of HF. Thereafter, values greater than 10 TPY of HF have been reported to EPA.³

² Paper. Nagy, J.M. and Hilakos, S.W., SF Phosphates. PECO Fluorine Removal Process Pilot Plant. AICHE Clearwater Convention. May 23, 1998.

³ EPA Website. Toxic Release Inventory. Accessed on August 4, 2002. www.epa.gov/triexplorer/facility.htm

Calculations submitted to the Wyoming Department of environmental quality indicate emissions of 15 tons of HF during 2001.⁴ Furthermore an application for an operation permit includes an emission estimate of HAPs of 22 tons per year of hydrogen chloride (HCl) and HF combined.⁵

A statement was included in the application as follows:

“Per the 40CFR63 applicability letter submitted to the division on 8/18/99, SFP did not believe that the Rock Springs fertilizer complex would be a major source under this NESHAP as the sources subject to this regulation do not emit more than 10 TPY of HF. However, it recently came to SFP’s attention that total facility emissions of HF must be considered when determining major source status. Therefore, we now believe that HF emissions from the phosphogypsum tailings area should be included in this facility’s major source determination even though this source is not specifically regulated by the NESHAP. The HF emissions from this source are estimated, but SFP believes these estimates to be scientifically based and reasonably accurate. By including these emissions with those emitted from NESHAP regulated sources, more than 10 TPY of HF is emitted on a facility-wide basis and thus, the NESHAP outlined under 40CFR63 is applicable to this newly constructed source.”

The Wyoming facility is smaller than the larger complexes in Florida.

⁴ Emission Inventory Calculations for SF Phosphates. Wyoming Department of Environmental Quality. Supplied to Florida DEP on July 24, 2002.

⁵ Application. SF Phosphates Rock Springs Fertilizer Complex. Operating Permit Application for New Phosphoric Acid Plant. November 20, 2000.



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PHONE: 224-8238

FAX: 224-8061

FROM: Al Linero

PHONE: 921-9523

Division of Air Resources Management

FAX: 850.922.6979

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Division of Air Resources Management

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