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SKEC 173-82-08

May 18, 1984

Mr. Clair Fancy
Florida Department of
Environmental Regulation
Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32301

Subject: Polk County - AP
USS Agri-Chemicals
Ft. Meade Chemical Complex PSD Application

Dear Mr. Fancy:

In partial response to your letter of February 21, 1984, I am forwarding, in its entirety, one of the references cited in the referenced PSD application and pertinent information from a second cited reference.

In the PSD application for the USSAC Chemical Complex, we cited correspondence from TRW related to fluoride emissions from process water cooling ponds in the phosphate fertilizer industry and a document published by EPA that contained vapor pressure data for fluoride over pond water. Attached hereto is a complete copy of the TRW interoffice correspondence prepared by Mr. Jack Preece and dated August 27, 1984. Mr. Preece is now with the FDER office in Pensacola.

We have never had a complete copy of EPA Document 650/2-74-095 and in the PSD application we only recited a reference to this document that was originally made in the above reference TRW correspondence. We have however, obtained, and are attaching hereto, a summary of the fluoride vapor pressure data contained in the referenced EPA document from a document entitled, Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry. This document was prepared for EPA under Contract No. 68-02-1330, Task No. 3 in 1976.

I trust that the enclosed information will satisfy your requirements for information related to these two references. If there are further questions regarding these references, please feel free to contact me.

Very truly yours,

SHOLTES & KOOGLER,
ENVIRONMENTAL CONSULTANTS

John B. Koogler, Ph.D., P.E.

JBK:ldh
Enclosures

cc: Mr. Jim Carroll

TRW
ENVIRONMENTAL ENGINEERING DIVISION

INTEROFFICE CORRESPONDENCE

1423.80.JWP.008

TO: File

CC:

DATE: August 27, 1980

Jack Preece

SUBJECT: Derivation of Emission Factors for Fluorides from Gypsum Ponds

FROM: Jack Preece

BLDG. RPNC MAIL STA. 100 EXT. 541-9100

In the PSD reviews for phosphate fertilizer plants, it is desirable to quantify the emissions of fluorides from the process cooling water ponds. The literature yields a wide range of emission factors (0.1 to 10 pounds fluoride per acre-day). The temperature dependence is not well accounted for if one tries to use a single emission factor for all pond size operating at various production rates (heat load). The following derivation determines an emission factor for the cooling gradient portion of any pond (used process water assumed to be 113°F entering the pond and cooled pond water assumed ready for reuse at 95°F leaving the pond). The ambient temperature of 92°F is assumed to be typical for southwest Florida.

I. VAPOR PRESSURE VS POND WATER TEMPERATURE

Reference 1 reviews vapor pressure determinations published by Tatera and by King and Ferrell (Reference 2). Both of these studies measured vapor pressure of fluoride above pond water in the range of 70°F to 100°F. Phosphate fertilizer plant cooling water ponds operate at about 95 to 112°F. Thus, the data must be extrapolated.

This author selected the data of King and Ferrell to best represent vapor pressure over pond water which was in equilibrium with pond bottom sediment. The data listed on pages 54-57 of Reference 2 when averaged in three groups is summarized as:

Temperature, °F	Fluorine Partial Pressure, (10^{-6} mm Hg)
79.79	414.33
90.01	395.4
100.16	665.94

The data for runs made near 70°F were not included since normal pond operating temperature rarely is that low. These 70°F runs had higher vapor pressure than the others and contribute to the concave shape of the curve. The three phase equilibrium mechanism offered by the authors to account for this unusual shape is interesting and undoubtedly accounts for these ponds stabilizing in fluoride concentration after continued use. The 70°F data is not pertinent to the development of an emission factor for ponds that operate above 95°F.

The authors fit smooth curves to their data by eye. These curves appear to be parabolical as plotted on semi-log scales. Therefore, this author fit the following empirical formula to the three data points.

$$\ln VP = a + bt + ct^2$$

or $$VP = \exp(a + bt + ct^2) \qquad \text{Equation 1}$$

By solution of simultaneous equations the values for the coefficients are:

$$a = 26.1131$$
$$b = -.470843$$
$$c = .00274598$$

II. EMISSION FACTOR VS VAPOR PRESSURE

Reference 2, page 104, offers the following equation for determining fluoride emissions:

$$N_f = K_f (P^* - P)$$

where $$K_f = 1.96 \times 10^3 \, u_{16}^{.8} \, \frac{\text{lb}}{\text{acre-day-mm Hg}}$$

u_{16} = wind velocity at 16 meter height, meters/second.

P^* = fluoride partial pressure from their curves (from equation derived above), mm Hg.

P = ambient air fluoride partial pressure (assumed as 0, since they never measured above 30×10^{-6} mm Hg in the field).

with u_{16} = 2.78 meters/second (1970-1974) average at Tampa, Florida airport) these equations reduce to:

$$N_f = 3.653 \times 10^{3} P^*$$

or $$N_f = 3.653 \times 10^{-3} VP \qquad \text{Equation 2}$$

since $p^* = 10^{-6} \times VP$ from Equation 1.

III. POND TEMPERATURE PROFILE

Reference 3 uses the following equation to determine area required to cool water:

$$\frac{t_i - t_a}{t_f - t_a} = \exp \frac{A}{K}$$

where

A is pond area, acres
t_i is initial temperature of water
t_f is final temperature of water
t_a is ambient air temperature
K is a function of water rate, mass transfer constant and conversion factors.

This can be transformed to:

$$A = K \log_e \frac{t_i - t_a}{t_f - t_a} \qquad \text{Equation 3}$$

which is the definite integral between the limits of t_i and t_f of:

$$dA = K \frac{dt}{t - ta} \qquad \text{Equation 4}$$

IV. EMISSION FACTOR FOR COOLING GRADIENT PORTION OF POND

The cooling gradient portion of the pond is that required to cool the process water from its initial temperature as it comes to the pond from the process (typically 113°F) to the final temperatures required for reuse in the process (typically 95°F). A worst case ambient temperature of 92°F is assumed.

The differential emissions are:

$$dE = dA \quad N_f$$

$$dE = \left(K \frac{dt}{t - ta}\right) \times \left(3.653 \times 10^{-3}\right) \times \left(\exp\left(a + Bt + ct^2\right)\right).$$

The total emissions over the cooling gradient portion are:

$$E = K \quad 3.653 \times 10^{-3} \int_{95}^{113} \frac{\exp\left(a + bt + ct^2\right) dt}{t - 92}$$

The approximate value of the integral was determined by Simpson's Rule using 0.25°F intervals to yield:

$$E = K \quad 3.653 \times 10^{-3} \times 1713.7$$

$$= K \quad 6.260 \frac{\text{lbs Fluoride}}{\text{day}}$$

The average emissions factor for this cooling gradient portion of a pond is:

$$N_f = \frac{E}{A} = \frac{K \quad 6.260}{K \quad \log_e \frac{113-92}{95-92}}$$

$$= 3.22 \frac{\text{lbs Fluoride}}{\text{acre-day}}.$$

K cancels out of this average emission factor determination. The evaluation of K for specific heat load and production rate is discussed in Section IV below.

V. EMISSION FACTOR FOR CONSTANT TEMPERATURE PORTION OF POND

The remainder of any size pond further assumes a temperature approaching equilibrium which ambient conditions. Since it is essentially constant it is assumed to be 93.5°F. Using equations 1 and 2, an emission factor is determined for 93.5°F as:

$$N_f \text{ @ } 93.5 = 1.62 \frac{\text{pounds fluoride}}{\text{acre-day}} .$$

VI. EFFECT OF PRODUCTION RATE ON HEAT LOAD

The specific area required for the gradient portion of a pond will vary proportionately with the heat load which is assumed to vary proportionately to the production capacity of phosphoric acid. The specific calculations of Reference 3 were for 13.21×10^6 cubic feet per day of water needed to produce 679,600 tons per year of P_2O_5. K of the equations in Section III for this specific use is:

$$K = \frac{62.4 \frac{\text{pounds water}}{\text{cu.ft.}} \quad 13.21 \times 10^6 \frac{\text{cu.ft.}}{\text{day}}}{215 \frac{\text{pounds water}}{\text{ft}^2 - \text{day}} \quad 43560 \frac{\text{ft}^2}{\text{acre}}} = 88.02 \text{ acres.}$$

The mass transfer coefficient of 215 was determined empirically for cooling water ponds.

For the typical temperatures assumed in Section IV the required area for this specific heat load is:

$$A = 88.02 \log_e \frac{113 - 92}{95 - 92} = 171 \text{ acres.}$$

This specific condition had a 413 acre cooling pond. Therefore, the constant temperature end of this pond was:

413 - 171 = 242 acres

The total fluoride emissions for this example will be:

E = 171 X 3.22 + 242 X 1.62 = 943 pounds Fluoride/day (172 tons/year).

REFERENCES

1. A. A. Linero and R. A. Baker, EPA 600/2-78-124, June 1978.

2. W. R. King and J. K. Ferrell, EPA-650/2-74-095, October 1974.

3. PSD-FL-067 Application submitted to EPA Region IV by Occidental Chemical Company, White Springs, Florida. Prepared by Sholtes and Koogler.

EVALUATION OF EMISSIONS AND CONTROL TECHNIQUES FOR REDUCING FLUORIDE EMISSIONS FROM GYPSUM PONDS IN THE PHOSPHORIC ACID INDUSTRY

Prepared by

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Contract No. 68-02-1330 Task No. 3

EPA Project Officer: Edward Wooldridge
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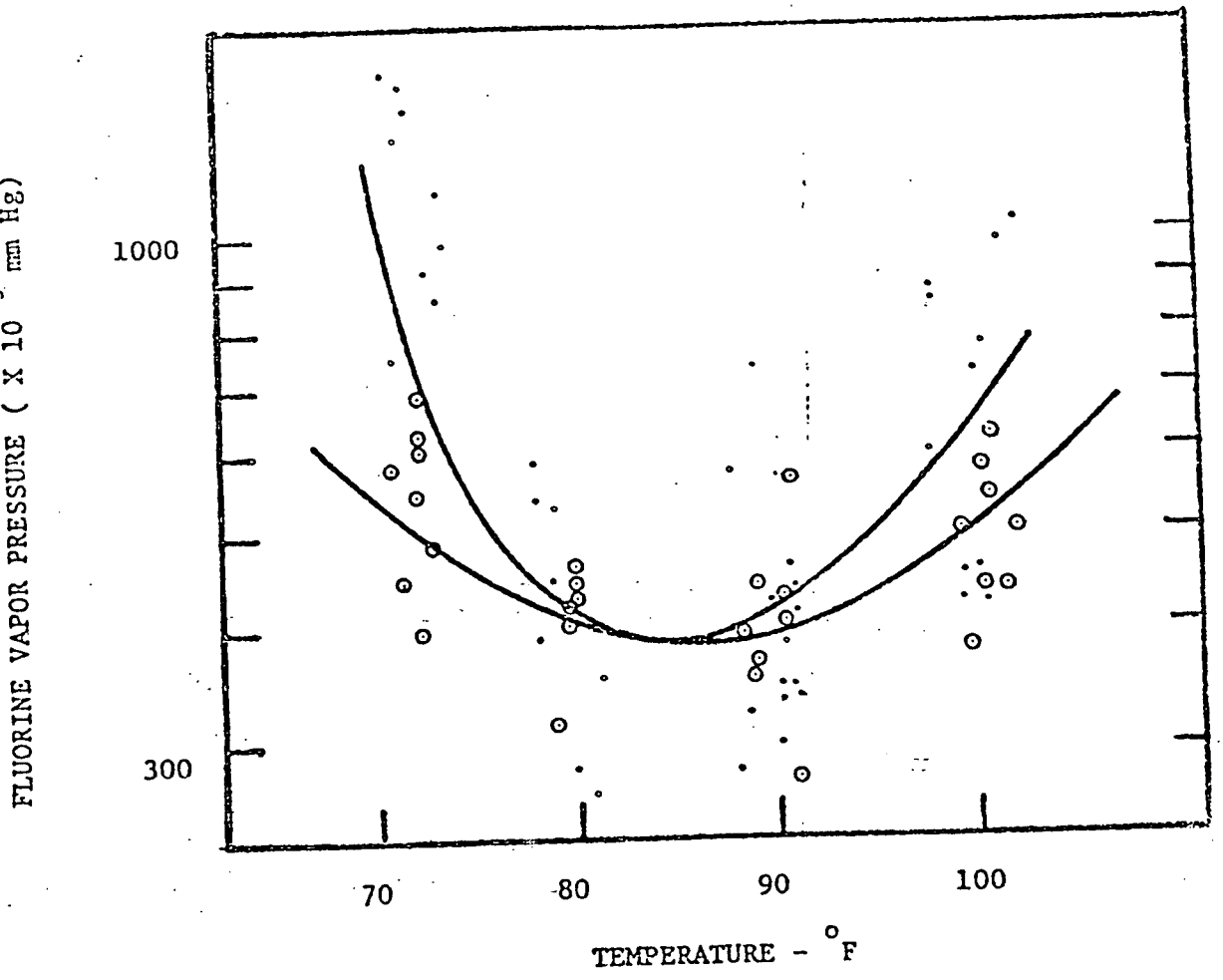

Figure 4.7. Fluorine Vapor Pressure Over Pond Water.
Source: King, 1974

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USS Agri-Chemicals
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August 20, 1984

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Subject: USS Agri-Chemicals
Ft. Meade Chemical Complex
Sulfuric Acid Plant & Phosphoric Acid Plant
Modifications, Concerning the PSD Application
Filed January 19, 1984

Dear Mr. Fancy:

In partial response to your letter of February 21, 1984, regarding constructions permits to modify two existing sulfuric acid plants and two existing phosphoric acid plants at the USS Agri-Chemicals (USSAC) Ft. Meade Chemical Complex technical information was forwarded to your office and received on May 21, 1984. The issues not addressed in our response received on May 21st were discussed during a meeting with your staff in Tallahassee on July 27, 1984, and are addressed herein.

On May 21, 1984, information from Sholtes & Koogler, Environmental Consultants (SKEF) was received in your office regarding documents referenced in the calculation of fluoride emissions from the process water cooling pond. The documents included TRW (an EPA Contractor) interoffice correspondence dated August 27, 1980 and sections of EPA document 650/2-74-095. It is our understanding that the information, as received in your office on May 21, 1984, satisfies the request in your letter of February 21, 1984 for information on that specific issue.

Regarding the other issues addressed in your correspondence of February 21, 1984, representatives of USSAC met with Mr. Willard Hanks in your offices on July 27, 1984 to discuss the specific information that would be required to provide your staff with the information they need to complete the review of the subject permit applications. Based upon this meeting, the following information is provided to complete the Construction Permit applications for the modifications to the sulfuric acid and phosphoric acid plants.

Permit Fees

An additional permit fee of $1,200 will be forwarded to the Tallahassee FDER offices by USSAC. This will complete the total fee of $2,200 required for the four permit applications; $1,000 for each of two sulfuric acid plants and $100 for each of two phosphoric acid plants.

Physical Modifications to the Sulfuric Acid Plants

In the permit applications for the revisions to the sulfuric acid plants, it was stated that certain physical modifications would be necessary. As discussed during the July 27, 1984 meeting, the details of these physical modifications are not now known and will not be known until detailed engineering is completed to determine just where bottlenecks might occur. The one physical change that will almost certainly be involved is an increase in the amount of catalyst in the converter of the sulfuric acid plant. Possible physical changes might also be required to increase the acid cooling capacity or to increase the acid recirculation rate within the plant. Equipment in the sulfuric acid plants that will least likely require modification include the demisters for acid mist control, the sulfur burner, the absorber, the cooling tower and the blower.

In summary, USSAC can only state that the physical modifications that will be required are expected to be minor in nature and will not be fully known until the existing plant is run up to its limit and debottlenecking engineering is completed. It can be stated, however, that none of the changes will effect compliance with New Source Performance Standards (NSPS) for the sulfuric acid plant.

Phosphoric Acid Plant Modifications

The actual physical modifications are not known at the present time. However, modifications may be needed when the installed capacity is run to its limit. Modifications will be necessary only if the P_2O_5 recovery proves to be uneconomical.

Gypsum Disposal Area

The life of the gypsum disposal area associated with phosphoric acid production is a function of the phosphoric acid production capacity of the USSAC Ft. Meade Chemical Complex. The modifications to the two phosphoric acid plants will result in an approximate 25 percent increase in the permitted production rates. If it is assumed that when the plants operate at a production capacity greater than presently permitted, the life of the gypsum disposal area will be decreased proportionately.

More germane to the subject permit applications is the wetted surface area on the gypsum disposal area and in the process water cooling ponds. The presently permitted wetted area in both the gypsum disposal area and the process water cooling pond is sufficient to provide the necessary cooling. There will be no increase in the wetted surface area on either the gypsum disposal area or the cooling ponds. The changes in fluoride emission rates from these wetted surface areas has been addressed in the permit application.

The information provided herein should complete the permit applications for the requested rate increases for the sulfuric acid and phosphoric acid plants at the USSAC Ft. Meade Chemical Complex. If additional information is required or if there are any questions regarding information contained herein, please do not hesitate to contact us.

Very truly yours,

USS AGRI-CHEMICALS

J. C. Daniel, Manager
Special Projects &
Environmental Engineering

JCD:myv

cc: Dr. J. B. Koogler