

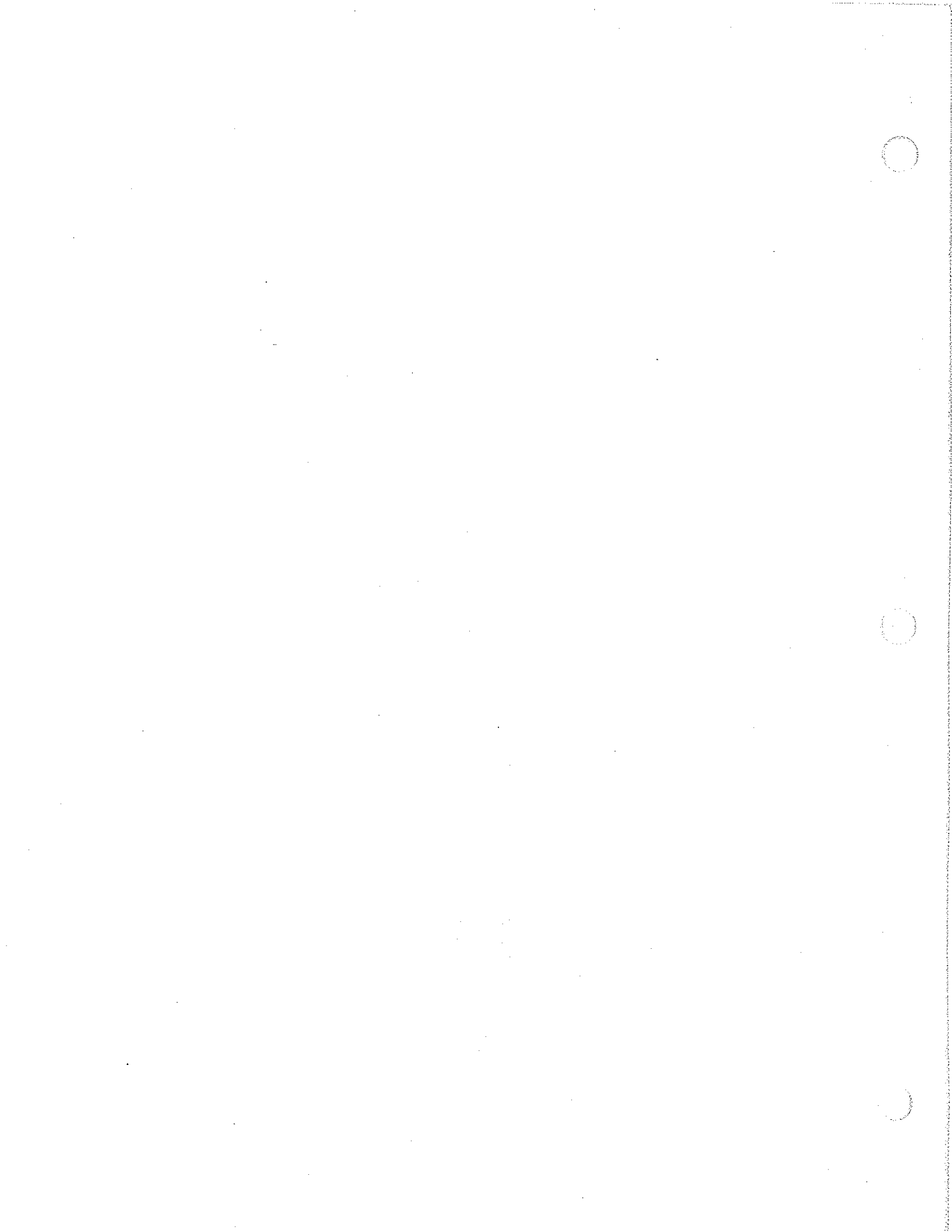
A COMPUTER MODEL for DETERMINING THE GRADE
of DIAMMONIUM PHOSPHATE from PHOSPHORIC ACID ANALYSIS

by

Conrad Hovik
Farmland Industries, Inc.
Bartow, Florida

Presented at the
Joint Meeting of the Central and Peninsular Sections
American Institute of Chemical Engineers

Clearwater Beach, Florida
5/25/85



Abstract

A great deal of recent work has been devoted to identifying the compounds that comprise agricultural grade diammonium phosphate. (ref 1,2,3) This paper describes a heuristic model that was developed to predict the grade of DAP (diammonium phosphate) from limited elemental analyses of the DAP feeds. The model design is based upon the actual analyses of nominal 18-46-0 DAP (diammonium phosphate) that was produced at the Farmland Industries facility coupled with compounds that are discussed in the referenced literature above. Discussion within the paper covers; the method used to develop the model, the structure of the model, testing, model predictions, problems and limitations.

Summary

A model was developed to predict the grade of DAP from elemental analyses of the feed acids and is based upon certain specific compounds predicted to exist in nominal DAP (ref 1,2,3). The technique used to design the model was to utilize the elemental analyses of DAP, together with the afore mentioned compounds, to predict its own grade through the model. This iterative technique assumes an elemental balance exists, prior to and after, the formation of compounds comprising nominal DAP. Error between predicted and actual grade fell below 0.85 % (approximately 0.15 wt% N and 0.39 wt% P2O5) for 11 sets of data. After design of the model was complete, elemental analyses of the nominal 30% and 54% acids were used in the model along with production totalizer data to test the ability to predict grade on a plant level. As expected, the confounding effects of using more than one analysis along with plant production data approximately doubled error to a value consistently less than 1.93 % (approximately 0.33 wt% N and 0.89 wt% P2O5). The model provides an inexpensive vehicle for gaining insight into the complex nature of DAP on a day to day basis without the time and expense of involved analytical techniques, ie., emission spectrometry, microscopic, x-ray and infrared techniques.

Discussion

Purpose -

In recent years the level of impurities present in phosphate rock used to produce FII (Farmland Industries Inc.) wet-process phosphoric acid has increased to a point where management of impurities is of paramount importance. One of the consequences of not dealing strategically with impurities in the process is off specification DAP. A great deal of time and money is expended in the phosphate industry just to deal with this problem. Everything from the mining plan and blending of the phosphate ore to the acid blend strength feeding the DAP plant revolve to a certain degree around impurity levels. Traditionally, several elements have been used to monitor the quality of rock entering the process, ie., P2O5, CaO, Fe, Al and Mg. The relationship between these impurities and grade had been observed for many years but the structure of the compounds formed was not clear. Frazier, et. al. (ref 3), obtained 26 different commercial samples of DAP and performed detailed chemical and crystallographic characterizations on them. Probable reasons for grade problems were presented as a function of these elemental characterizations and some process parameters. This work is the basis for the design of the model. Table 1 below summarizes the major compounds presented in the above referenced work that are considered in the model.

The purpose of the model was to predict DAP grade through elemental analyses while using the above mentioned compounds as constraints within the system. If this could be accomplished then we would have an inexpensive method for providing regular feedback to production and management, circumventing the involved and costly analyses now needed for multielement determinations. Basically, this is an empirical approach to predicting grade.

†
Table 1

Ca ₄ SiAl ₅ O ₄ F ₁₃ * 10H ₂ O	FeNH ₄ (HP ₀₄) 2	(NH ₄) H ₂ PO ₄
ZnNH ₄ PO ₄	AlNH ₄ (HP ₀₄) 2	(NH ₄) 2HP ₀₄
CdNH ₄ PO ₄	FeNH ₄ HP ₀₄ F ₂ * H ₂ O	(NH ₄) 3PO ₄
UO ₂ NH ₄ PO ₄	AlNH ₄ HP ₀₄ F ₂ * H ₂ O	(NH ₄) 2SiF ₆
NiNH ₄ PO ₄	VNH ₄ HP ₀₄ F ₂	(NH ₄) 2SO ₄
MnNH ₄ PO ₄	CrNH ₄ HP ₀₄ F ₂	NaH ₂ PO ₄
MgNH ₄ PO ₄ * 6H ₂ O	Ca (NH ₄) 2 (HP ₀₄) 2 * H ₂ O	KH ₂ PO ₄
		free H ₂ O

+ note that water of hydration may vary.

Model Development and Testing -

Farmland Industries produces nominal 18-46-0 DAP in a conventional preneutralizer/granulator plant. All 30 wt% P₂O₅ acid is fed to a recycle tank which is common to the dryer, screen/mill, and reactor/granulator scrubbers. This acid, ammoniated to a 0.8 mole ratio, is fed forward along with 54% P₂O₅ acid to the preneutralizer resulting in a net 37 wt% P₂O₅ blend to the plant. Acid in the preneutralizer is further ammoniated to a 1.52 mole ratio. This reactor operates at 255 deg F, a specific gravity of 1.58 to 1.60 and a retention time of approximately two hours. Slurry from the preneutralizer is fed to the granulator where it is mixed with recycle at a 6/1 ratio and ammoniated to a 1.98 mole ratio. Granulator discharge is dried to a free moisture content of 1.5% H₂O in a 11 ft by 80 ft cocurrent rotary drum dryer. All dryer discharge material is screened. Product is removed, cooled in a countercurrent fluid bed cooler and sent to storage. All oversized material is crushed in cage mills, combined with undersize and additional on size material, and returned as recycle to the granulator.

Composite samples were taken of nominal 30 wt% and 54 wt% acid feeds along with the DAP that was produced. These three types of samples comprise a set. A total of 12 sets were taken with the twelfth being discarded due to process and production problems encountered that particular day. Sets 1 through 8 represent 24 hour composites and sets 9 through 11, 8 hour composite samples. Table 2 below shows the elemental analyses for the DAP products. Similar analyses were performed for the nominal 30 wt% and 54 wt% P₂O₅ acids.

When moving from acids to products many confounding and synergistic effects occur which impede efforts to predict the grade of DAP. For simplicity I refer to these items as noise. Some of these are listed below.

- a. Small amounts of fluorine, silicon and ammonia are given off during reaction.
- b. Tank strappings and totalizer readings have inherent inaccuracies.
- c. Laboratory analyses for acids and product have limited precision and accuracy.
- d. Miscellaneous process problems occur.

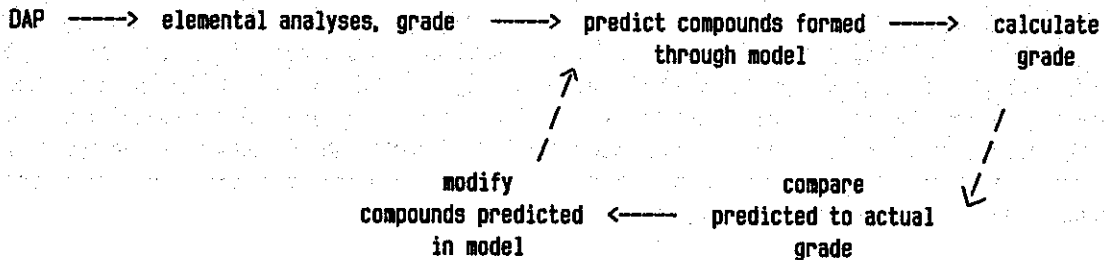
nominal 30 wt% phos acid noise
 nominal 54 wt% phos acid -----> nominal DAP
 ammonia

Table 2
DAP Elemental Analyses

Weight %

set	P2O5	N	SO4	Al2O3	Fe2O3	F	CaO	MgO	SiO2	Na2O	K2O
1	45.77	17.15	4.35	1.98	2.03	2.24	0.71	0.43	0.72	0.26	0.11
2	45.65	17.17	4.72	1.89	2.10	2.48	0.61	0.45	0.70	0.25	0.10
3	46.00	17.71	3.87	1.64	1.21	2.13	0.70	0.43	0.95	0.20	0.09
4	46.22	17.89	4.01	1.65	1.39	2.38	0.77	0.51	0.85	0.22	0.08
5	46.21	17.93	3.72	1.47	1.37	2.32	0.60	0.48	0.78	0.21	0.08
6	46.18	17.94	4.54	1.60	1.41	2.20	0.58	0.49	0.76	0.17	0.07
7	46.13	17.97	3.95	1.53	1.33	2.81	0.71	0.52	0.81	0.18	0.08
8	46.13	17.91	3.84	1.58	1.27	2.63	0.73	0.54	0.85	0.22	0.07
9	46.60	18.10	3.80	1.30	1.39	2.67	0.71	0.54	0.73	0.19	0.06
10	46.44	18.09	3.75	1.68	1.17	2.84	0.68	0.50	0.66	0.20	0.08
11	46.46	17.98	4.42	1.63	1.18	2.89	0.67	0.49	0.72	0.19	0.08

To eliminate the problems associated with noise, design of the model was based solely on the DAP elemental analyses. Later, after the model was completed, acid analyses would be fed into the model to predict DAP grade. The figure below illustrates the iterative method used to develop the model.



An implicit assumption imbedded in the FII model is an elemental balance, i.e., all major elements analyzed for in the actual DAP are carried forward through the model and are present in the predicted DAP. This implies that all elements present in the DAP when it was analyzed were present in the feed acids. This assumption allows dissection of DAP to primary elements, ex., Fe, Al, Mg, F, etc. Once scrambled, the DAP analyses can be fed through the model algorithm to reconstruct the compounds that make up the DAP. The method is akin to taking a picture, making a jig saw puzzle out of it, scrambling the pieces and running them through a black box to reconstruct the puzzle. An important limitation here is the quality of the original picture. If the analyses of the components making up the DAP are of questionable accuracy or not analyzed for, the result is a hazy beginning picture. Consequently, reconstruction through the algorithm will be hazy. Complete and accurate analyses are always needed. N.B., it is conceded that all elements present in the acid do not carry forward to DAP, ex., F and Si. However, the vast majority of mass is conserved and therefore the assumption is considered to be a valid one.

The basic design algorithm is as follows.

1. Basis of 1.0 lb DAP.
2. Based upon elemental analyses of DAP calculate the number of moles of each element, Fe, Al, Si, P, N, etc., available for reaction.
3. React each element one by one according to the following precedence order.
 - Mg ----> $MgNH_4PO_4 \times 6H_2O$
 - Ca ----> $Ca_4SiAlSO_4F_{13} \times 10H_2O$ & $Ca(NH_4)_2(PO_4)_2 \times H_2O$
 - SO₄ ----> $(NH_4)_2SO_4$
 - Si ----> $(NH_4)_2SiF_6$
 - Na, K ----> NaH_2PO_4 & KH_2PO_4
 - Zn, Cd, U, Ni, Mn ----> $ZnNH_4PO_4$, $CdNH_4PO_4$, $UO_2NH_4PO_4$, $NiNH_4PO_4$ & $MnNH_4PO_4$
 - V, Cr ----> $VNH_4PO_4F_2$ & $CrNH_4PO_4F_2$
 - Al ----> $AlNH_4HPO_4F_2 \times H_2O$ (limited by amount of F left)
 - Fe ----> $FeNH_4HPO_4F_2 \times H_2O$ (limited by amount of F left)
 - Fe ----> $FeNH_4(HPO_4)_2$ (limited by amount of Fe left)
 - Al ----> $AlNH_4(HPO_4)_2$ (limited by amount of Al left)
 - P, N ----> $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3PO_4$calculate free H₂O

Some elements, like Mg, Si, SO₄, Na, K, Zn, etc., are easy to react to products since they form a single compound and/or involve only P and N which are present in liberal amounts and therefore would not limit the reaction. Ca is present in the form of two compounds, chukhrovite ($Ca_4SiAlSO_4F_{13} \times 10H_2O$) and $Ca(NH_4)_2(PO_4)_2 \times H_2O$. The assumption was made that 0.2 mole fraction of Ca is already present as chukhrovite with the balance forming $Ca(NH_4)_2(PO_4)_2 \times H_2O$. Minor components such as Zn, Cd, U, Ni, Mn, V and Cr are present in DAP in small amounts. Therefore, to lessen the number of analyses and calculations needed, these compounds were grouped together as $(M+)NH_4PO_4F_2$ at the following ratio, 1.18×10^{-5} lb-moles compound per pound of DAP formed. At this point in the algorithm, about half of the available fluorine has been consumed. According to Frazier, et. al. (3), the formation of the Al and Fe compounds depends to a great extent upon the amount of fluorine available for reaction. He delineates a specific precedence ordering regarding these four compounds listed in Table 1.

"Iron and aluminum also can precipitate as $(Fe, Al)NH_4(HPO_4)_2$ when there is insufficient fluorine in the phosphoric acid to precipitate $(Al, Fe)NH_4HPO_4F_2 \times xH_2O$. The Al end member precipitates first; the Fe end member precipitates if sufficient fluorine is present. If insufficient fluorine is present, the Fe end member of the compound $(Fe, Al)NH_4(HPO_4)_2$ precipitates first, with the Al end member precipitating next."

Hence, when reacting to form these compounds, a constant tally of the amount of fluorine used for each is necessary.

All that should remain at this point is phosphorus and nitrogen ready to react to form monoammonium phosphate (MAP), diammonium phosphate (DAP) and triammonium phosphate (TAP), which has been observed confirming earlier findings. (3) By adjusting the relative amounts of these compounds the N:P mole ratio can be changed. DAP appears to exist with either MAP or TAP but does not appear to exist with both at the same time. Hence, it is a simple matter to algebraically solve for the amount TAP and DAP that needs to be present to satisfy the known amounts of N and P left. If the mole ratio of nitrogen to phosphorus left at this point is greater than 2.0, then a mixture of TAP and DAP will be present, if it is less than 2.0 then MAP and DAP will be present and if it is equal to 2.0 then only DAP will exist. Recall that we are working from DAP elemental analyses, where the exact amount of nitrogen and phosphorus are known. The convenience of knowing both the amount of N and P left to react to MAP,

DAP and TAP is not present when working from feed acids since there basically is an infinite source of nitrogen available for reaction. An unexpected correlation appears to be present here that can be used to predict the presence of TAP when using acid feed analyses. The moles of $\text{AlNH}_4(\text{HPO}_4)_2$ present correlate to the moles $(\text{NH}_4)_3\text{PO}_4$ (TAP) formed according to the equation;

$$Y = 0.8069 X + 1.96 \times 10^{-5} \quad \text{where; } Y [=] \text{ moles } \text{AlNH}_4(\text{HPO}_4)_2 \\ X [=] \text{ moles } (\text{NH}_4)_3\text{PO}_4.$$

If the amount of TAP predicted from the equation is negative then it is assumed that MAP is formed as a constant mole fraction of the P left for reaction.

The moles of each compound to be formed are now known, hence the total mass present can be calculated and should approach the basis of 1.0 lb defined at the start of the design. The mass of moisture present can now be calculated and added to the total mass. One would suspect that at this point the mass generated should be slightly less than 1.0 lb due to incomplete analyses and in fact, this is the case. Values for the amount of mass missing varied from .003 to .030 lbs. This missing mass seems to correlate well with the mole ratio $(\text{Fe} + \text{Al})/(\text{F})$. The relationship can be described with the following equation.

$$Y = 9.53 X + .277 \quad \text{where; } Y [=] (\text{Fe} + \text{Al})/(\text{F}) \\ X [=] \text{ missing mass, lbs}$$

After the missing mass is approximated using the correlation above, the amount of water present can be recalculated.

The mass of each component making up the nominal DAP and the total mass are now known and from these values the weight % N and % P205 can be calculated. Table 3 outlines the results of using DAP analyses for design of the algorithm. As can be seen in Figures 1 and 2, the model generally follows actual grade quite well. Predicted grade consistently fell within 0.15 wt% N and 0.39 wt% P205 of actual for an error of less than 0.85 %. However, could the model now reasonably predict grade from elemental acid analyses and production data?

Model Predictions from Elemental Acid Analyses -

After the afore mentioned design and testing of the model using DAP elemental analyses, the elemental analyses of the 30 wt% and 54 wt% acids, along with totalizer data to calculate blend strengths, were fed to the model to predict grade. As might be expected the error was higher than with using only DAP analyses. Table 4 outlines the results. Figures 3 and 4 describe the results graphically.

Model error between actual and predicted grade when using acid elemental analyses was consistently less than 0.33 wt% N and 0.89 wt% P205 for an actual error of less than 1.92 %. This is in part due to the fact that DAP analyses were used to design and test the algorithm. Also, the fact that two separate analyses were used along with production totalizer data, make the combined elemental analyses of the acid feed inherently less accurate and precise. It is readily apparent from Figures 1 through 4 that even though the relative levels of error of N and P205 are about equal, P205 is much more sensitive to changes in impurity level, i.e., 1.0% change in grade is equal to about 0.46 weight % P205 and only 0.17 weight % N.

To illustrate the utility of the model, results from two of the eleven sets are shown below as they appear in the computer printout. (see Figures 5 and 6) Compounds are listed on the left with lb-moles

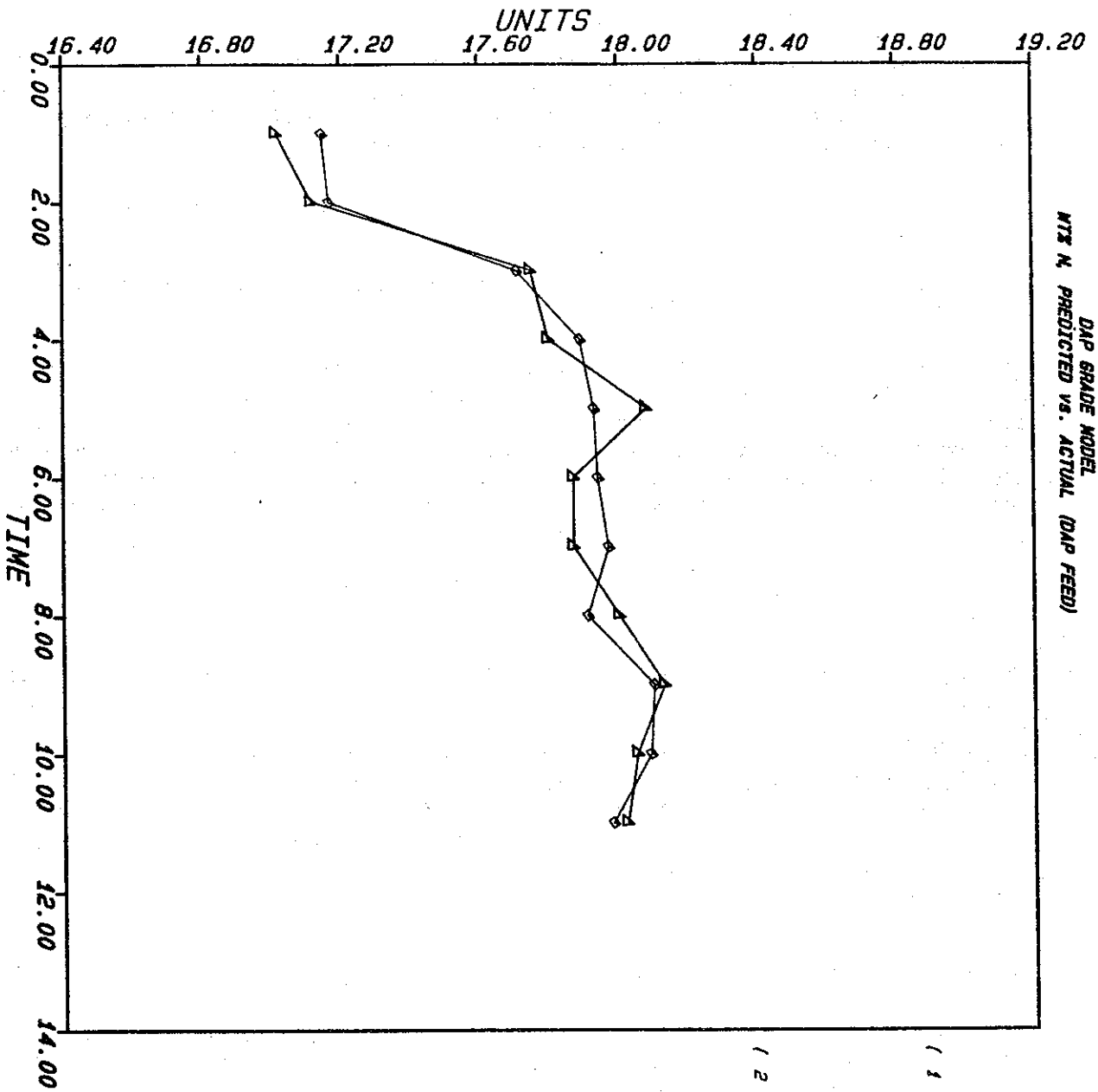


FIGURE 1
DAP GRADE MODEL
MTX N PREDICTED vs. ACTUAL (DAP FEED)

(1 / 1 /85 11/11 /85

Tab Report #5003

(1) Δ PREDICTED MTX N

(2) ◇ ACTUAL MTX N

TOTAL SUM 195.71
 AVERAGE 17.79
 STD DEV 0.36
 MAXIMUM 18.13
 MINIMUM 17.02
 CASES 11.00

TOTAL SUM 195.84
 AVERAGE 17.80
 STD DEV 0.32
 MAXIMUM 18.10
 MINIMUM 17.15
 CASES 11.00

12-11-85
16.03.03

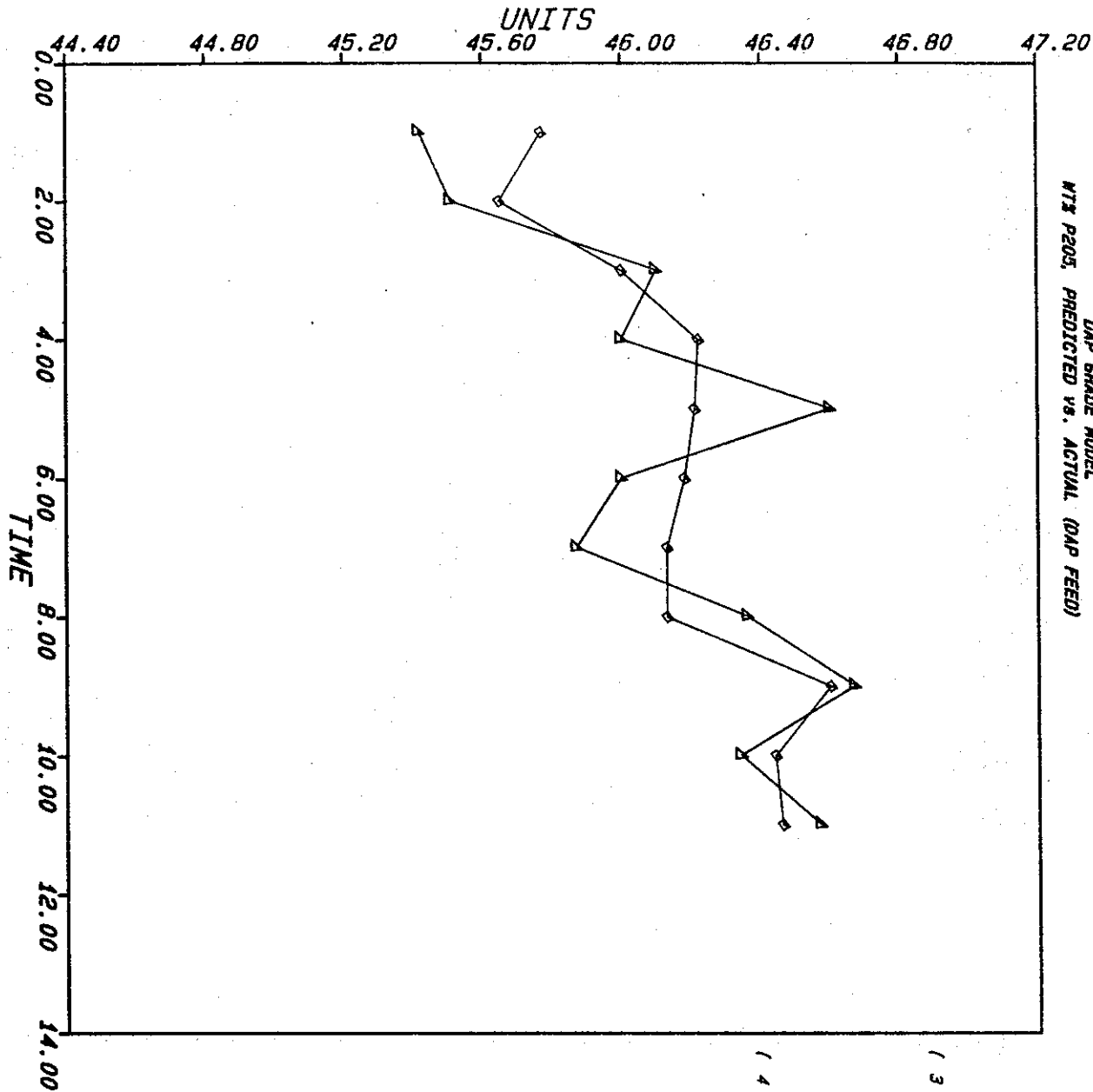


FIGURE 2
DAP GRADE MODEL
WTX P205, PREDICTED vs. ACTUAL (DAP FEED)

(1 / 1 / 85 ENJU 1 / 11 / 85

Tad Report #6004

(3) A PREDICTED WTX P205

(4) B ACTUAL WTX P205

TOTAL SUM	507.44
AVERAGE	46.13
STD DEV	0.40
MAXIMUM	46.67
MINIMUM	45.42
CASES	11.00
TOTAL SUM	507.79
AVERAGE	46.16
STD DEV	0.27
MAXIMUM	46.60
MINIMUM	45.65
CASES	11.00

12-APR-85
16:06:11

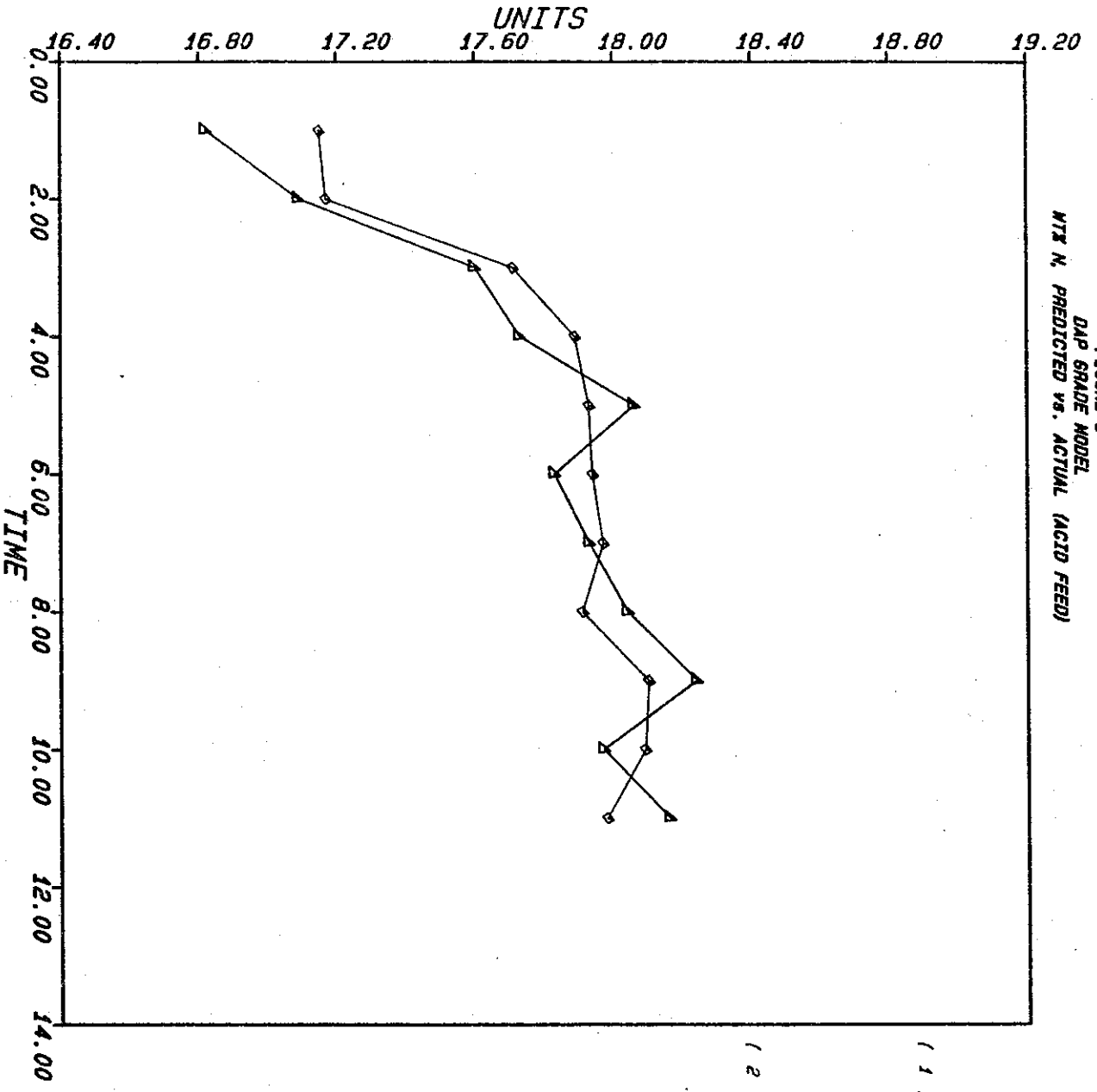


FIGURE 3
DAP GRADE MODEL
WT% N, PREDICTED VS. ACTUAL (ACID FEED)

(1 / 1 / 85 thru 1 / 11 / 85

Tab Report #6001

(1) Δ PREDICTED WT% N

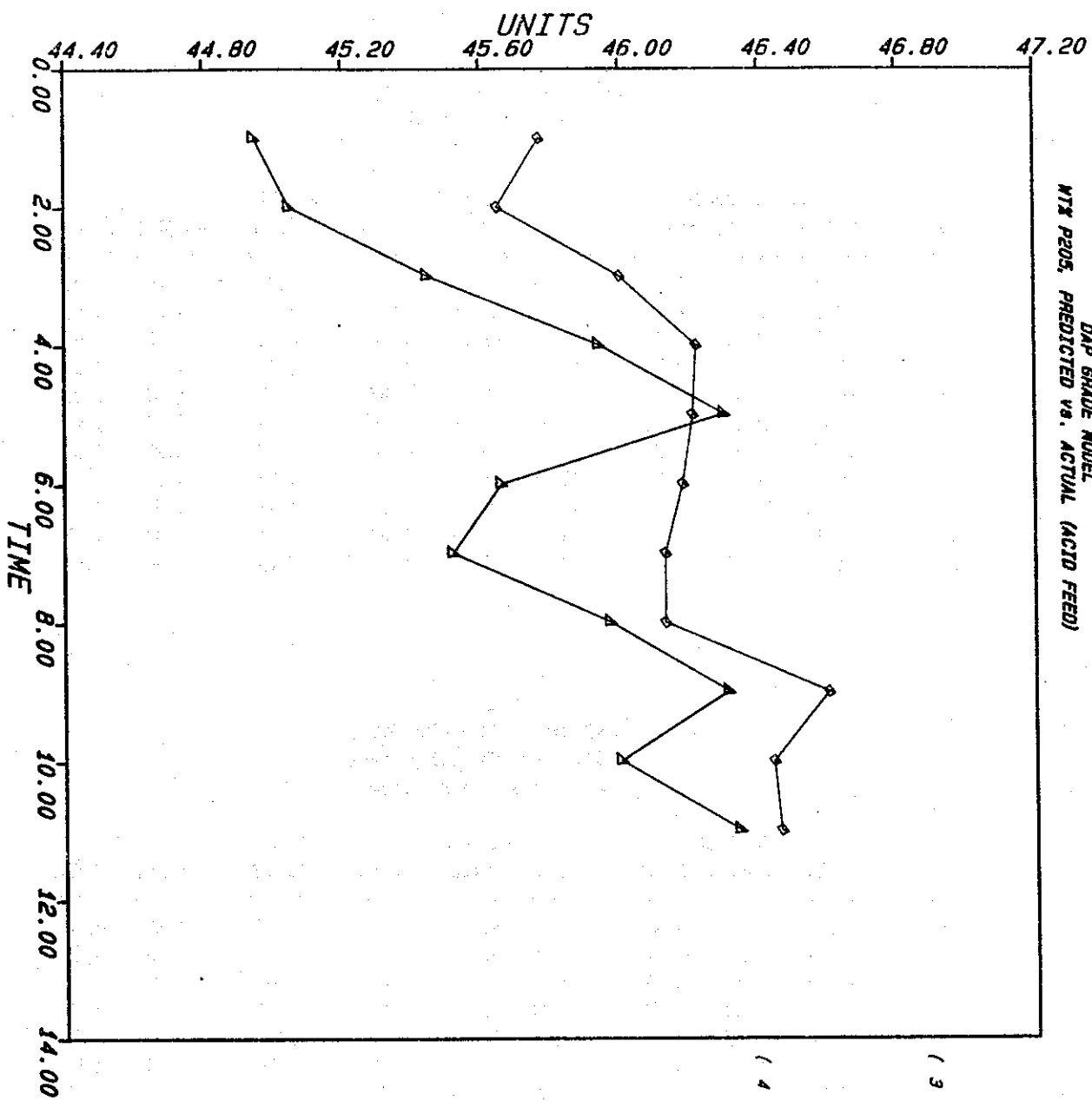
TOTAL SUM 195.47
 AVERAGE 17.77
 STD DEV 0.43
 MAXIMUM 18.24
 MINIMUM 16.82
 CASES 11.00

(2) ◇ ACTUAL WT% N

TOTAL SUM 195.84
 AVERAGE 17.80
 STD DEV 0.32
 MAXIMUM 18.10
 MINIMUM 17.15
 CASES 11.00

12-APR-85
 16:08:12

FIGURE 4
DAP GRADE MODEL
WTX P205, PREDICTED vs. ACTUAL (ACID FEED)



(3) / (1 / 85 thru 1 / 11 / 85

Tab Report #6002

(3) Δ PREDICTED WTX P205

TOTAL SUM 503.49
 AVERAGE 45.77
 STD DEV 0.47
 MAXIMUM 46.34
 MINIMUM 44.95
 CASES 11.00

(4) ◇ ACTUAL WTX P205

TOTAL SUM 507.79
 AVERAGE 46.16
 STD DEV 0.27
 MAXIMUM 46.60
 MINIMUM 45.65
 CASES 11.00

12-APP-85
 12:52:30

TABLE 3
DIAMMONIUM PHOSPHATE GRADES
DESIGN, USING DAP AS FEED
(basis 1.0 lb DAP)

set	wt% NITROGEN			wt% P2O5			wt% H2O ACTUAL	N/P	
	PREDICT	ACTUAL	%ERROR	PREDICT	ACTUAL	%ERROR		PREDICT	ACTUAL
1	17.02	17.15	-0.76	45.42	45.77	-0.76	1.74	1.90	1.90
2	17.12	17.17	-0.29	45.51	45.65	-0.31	1.35	1.91	1.91
3	17.75	17.71	0.23	46.10	46.00	0.22	2.59	1.95	1.95
4	17.80	17.89	-0.50	46.00	46.22	-0.48	1.97	1.96	1.96
5	18.08	17.93	0.84	46.60	46.21	0.84	1.57	1.97	1.97
6	17.87	17.94	-0.39	46.00	46.18	-0.39	1.58	1.97	1.97
7	17.87	17.97	-0.56	45.87	46.13	-0.56	2.45	1.97	1.97
8	18.00	17.91	0.50	46.36	46.13	0.50	1.57	1.97	1.97
9	18.13	18.10	0.17	46.67	46.60	0.15	1.38	1.97	1.97
10	18.05	18.09	-0.22	46.34	46.44	-0.22	1.71	1.97	1.97
11	18.02	17.98	0.22	46.57	46.46	0.24	0.82	1.96	1.96

TABLE 4
DIAMMONIUM PHOSPHATE GRADES
PREDICT, USING ACID AS FEED
(basis 1.0 lb blend acid)

set	wt% NITROGEN			wt% P2O5			wt% H2O ACTUAL	N/P	
	PREDICT	ACTUAL	%ERROR	PREDICT	ACTUAL	%ERROR		PREDICT	ACTUAL
1	16.82	17.15	-1.92	44.95	45.77	-1.79	1.74	1.90	1.90
2	17.09	17.17	-0.47	45.05	45.65	-1.31	1.35	1.92	1.91
3	17.60	17.71	-0.62	45.45	46.00	-1.20	2.59	1.96	1.95
4	17.73	17.89	-0.89	45.94	46.22	-0.61	1.97	1.95	1.96
5	18.06	17.93	0.73	46.30	46.21	0.19	1.57	1.98	1.97
6	17.83	17.94	-0.61	45.66	46.18	-1.13	1.58	1.98	1.97
7	17.93	17.97	-0.22	45.52	46.13	-1.32	2.45	1.99	1.97
8	18.04	17.91	0.73	45.97	46.13	-0.35	1.57	1.99	1.97
9	18.24	18.10	0.77	46.31	46.60	-0.62	1.38	2.00	1.97
10	17.97	18.09	-0.66	46.00	46.44	-0.95	1.71	1.98	1.97
11	18.16	17.98	1.00	46.34	46.46	-0.26	0.82	1.99	1.96

of each impurity contained in each compound following to the right. Column 13 gives the lb-moles of each compound formed and column 14 the mass. (Please note that lb-moles are times (10)⁵ while mass is times (10)³) Figure 5 shows the results from a low grade, low mole ratio product and Figure 6 the results from a high grade high mole ratio product (sets 2 & 5 respectively). Comparing the two it is immediately noticeable that the starting levels of impurities present in the low grade results are higher in every element, save magnesium. (see Available row) Aluminum and iron are higher by 40%

FIGURE 5

DAP GRADE MODEL
basis = 1# blend acid

Predicted
#moles (10)5

compound name	H2O	SO4	F	Fe	Si	Ca	Al	Mg	Na	K	PO4	N	Compd	lbs (10)3
Available	0.00	38.39	115.23	21.00	6.35	9.17	33.37	8.84	3.07	1.02	516.85	0.00		
MgNH4PO4.6H2O	53.05	0.00	0.00	0.00	0.00	0.00	0.00	8.84	0.00	0.00	8.84	8.84	8.84	21.70
Ca4SO4AlSiF13.10H2O	4.65	0.47	6.05	0.00	0.47	1.86	0.47	0.00	0.00	0.00	0.00	0.00	0.47	3.44
(NH4)2SO4	0.00	37.92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	75.84	37.92	50.09
FeNH4HPO4F2.H2O	4.02	0.00	8.04	4.02	0.00	0.00	0.00	0.00	0.00	0.00	4.02	4.02	4.02	9.08
AlNH4HPO4F2.H2O	32.91	0.00	65.82	0.00	0.00	0.00	32.91	0.00	0.00	0.00	32.91	32.91	32.91	64.83
(NH4)2SiF6	0.00	0.00	35.32	0.00	5.89	0.00	0.00	0.00	0.00	0.00	0.00	11.77	5.89	10.49
FeNH4(HPO4)2	0.00	0.00	0.00	16.98	0.00	0.00	0.00	0.00	0.00	0.00	33.97	16.98	16.98	45.14
AlNH4(HPO4)2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca(NH4)2(HPO4)2.H2O	7.31	0.00	0.00	0.00	0.00	7.31	0.00	0.00	0.00	0.00	14.62	14.62	7.31	20.91
(Mg)NH4PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.96	0.96	0.96	1.87
NaH2PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.07	0.00	3.07	0.00	3.07	3.69
KH2PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.02	1.02	0.00	1.02	1.39
NH4H2PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.29	7.29	7.29	8.39
(NH4)2HPO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	410.15	820.31	410.15	541.81
(NH4)3PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2O	61.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	61.00	10.99
unaccounted for	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.45
Total	162.94	38.39	115.23	21.00	6.35	9.17	33.37	8.84	3.07	1.02	516.85	993.54	597.83	814.27

Apparent Molecular Weight 136.20

Predicted Grade 17.09-45.05-1.35 N/P = 1.92

Actual Grade 17.17-45.65-1.35 N/P = 1.91

Predicted Impurities 698.2 #imp/ton P2O5

Actual Impurities 648.6 #imp/ton P2O5

ANALYSIS of FEED ACIDS and PRODUCT

tons P2O5 fed as 30% acid = 347.

tons P2O5 fed as 54% acid = 458.

tons (NH4)2SO4 added = 0.

tons H2SO4 added = 0.

wt%

compound name	P2O5	F	CaO	MgO	Fe2O3	Al2O3	SO4	SiO2	N	Na2O	K2O
30% acid fed to DAP	27.81	2.28	0.29	0.27	1.28	1.27	3.01	0.55		0.13	0.07
54% acid fed to DAP	48.37	2.07	0.81	0.47	2.20	2.27	4.58	0.16		0.27	0.13
Actual DAP Product	45.65	2.48	0.61	0.45	2.10	1.89	4.72	0.70	17.17	0.25	0.10

FIGURE 6

DAP GRADE MODEL
basis = 1# blend acid

Predicted
#moles (10)5

compound name	H2O	SO4	F	Fe	Si	Ca	Al	Mg	Na	K	PO4	N	Compd	lbs (10)3
*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
Available	0.00	31.67	103.25	13.78	5.99	8.62	23.81	9.60	2.87	0.81	523.80	0.00		
MgNH4PO4.6H2O	57.63	0.00	0.00	0.00	0.00	0.00	0.00	9.60	0.00	0.00	9.60	9.60	9.60	23.57
Ca4SO4A1SiF13.10H2O	4.38	0.44	5.69	0.00	0.44	1.75	0.44	0.00	0.00	0.00	0.00	0.00	0.44	3.23
(NH4)2SO4	0.00	31.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	62.47	31.24	41.26
FeNH4HPO4F2.H2O	8.76	0.00	17.51	8.76	0.00	0.00	0.00	0.00	0.00	0.00	8.76	8.76	8.76	19.78
AlNH4HPO4F2.H2O	23.37	0.00	46.74	0.00	0.00	0.00	23.37	0.00	0.00	0.00	23.37	23.37	23.37	46.04
(NH4)2SiF6	0.00	0.00	33.31	0.00	5.55	0.00	0.00	0.00	0.00	0.00	0.00	11.10	5.55	9.89
FeNH4(HPO4)2	0.00	0.00	0.00	5.02	0.00	0.00	0.00	0.00	0.00	0.00	10.04	5.02	5.02	13.34
AlNH4(HPO4)2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca(NH4)2(HPO4)2.H2O	6.87	0.00	0.00	0.00	0.00	6.87	0.00	0.00	0.00	0.00	13.75	13.75	6.87	19.66
(Mg)NH4PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.95	0.95	0.95	1.84
NaH2PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.87	0.00	2.87	0.00	2.87	3.44
KH2PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.81	0.81	0.00	0.81	1.11
NH4H2PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.29	7.29	7.29	8.39
(NH4)2HPO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	446.37	892.75	446.37	589.66
(NH4)3PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2O	69.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	69.96	12.61
unaccounted for	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.13
Total	170.96	31.67	103.25	13.78	5.99	8.62	23.81	9.60	2.87	0.81	523.80	1035.05	619.09	802.95

Apparent Molecular Weight 129.70

Predicted Grade 18.06-46.30-1.57 N/P = 1.98

Actual Grade 17.93-46.21-1.57 N/P = 1.97

Predicted Impurities 544.8 #imp/ton P2O5

Actual Impurities 557.8 #imp/ton P2O5

ANALYSIS of FEED ACIDS and PRODUCT

tons P2O5 fed as 30% acid = 397.
tons P2O5 fed as 54% acid = 434.
tons (NH4)2SO4 added = 2.
tons H2SO4 added = 0.

wt%

compound name	P2O5	F	CaO	MgO	Fe2O3	Al2O3	SO4	SiO2	N	Na2O	K2O
*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
30% acid fed to DAP	28.58	2.17	0.37	0.30	0.85	0.96	2.19	0.50		0.14	0.05
54% acid fed to DAP	51.28	1.62	0.67	0.53	1.51	1.63	4.27	0.13		0.24	0.12
Actual DAP Product	46.21	2.32	0.60	0.48	1.37	1.47	3.72	0.78	17.93	0.21	0.08

and 52% respectively while the amount of available fluorine increased a modest 12%. One would tend to predict from this information alone that grade would be poorer, but which compounds are going to form and in what amounts? As previously discussed, the relative amounts of all the Fe and Al compounds are a function of available fluorine. Since there is more aluminum and it reacts before iron when forming the di-fluoro compounds, the relative amounts of $\text{AlNH}_4\text{HPO}_4\text{F}_2 \cdot \text{H}_2\text{O}$ and $\text{FeNH}_4\text{HPO}_4\text{F}_2 \cdot \text{H}_2\text{O}$ should change. The mole ratio of $(\text{AlNH}_4\text{HPO}_4\text{F}_2)/(\text{FeNH}_4\text{HPO}_4\text{F}_2)$ moved from 2.7 in the high grade case to 8.2 for the low grade case. The rest of the available Fe goes to form $\text{FeNH}_4(\text{HPO}_4)_2$, Haseman-E (ref 4), which increased from 5.02 lb-moles to 16.98 lb-moles for the high and low grade cases respectively. Achorn, et. al. (1), describe the general effect of Al, Fe and other impurities and predict that if the total amount of Fe and Al present as Fe_2O_3 and Al_2O_3 is more than 3.0 wt%, the N grade will rapidly fall off from 18.0 wt%. Predicted values for combined Fe_2O_3 and Al_2O_3 were 4.2 wt% and 2.9 wt% for low and high grade respectively. The amount of almost every impurity compound predicted increased in the case of low grade. Formation of impurity compounds other than those just described above is straight forward and it is left to the reader to determine their effect and utility. Finally, since there are more impurities present to react with N and P in the low grade case than in the high grade case, it can be seen that the actual amounts of MAP, DAP and TAP formed in the low case were less. The final grade can be described superficially in terms of elemental impurity levels but is in actuality a function of the types of compounds formed from the elements and their respective masses.

Problems and Limitations -

The model does not exactly reconstruct DAP, but it will reasonably predict about where grade will fall and provide some insight to the mechanism that causes the resultant grade. Several items need to be noted. First, the MAP-DAP-TAP mix is estimated from a correlation linking the compound $\text{AlNH}_4(\text{HPO}_4)_2$ to the mix. However, this aluminum compound is a function of available fluorine. Is the correlation a coincidence and is the mix more a function of process parameters as discussed by TVA (ref 3)? Secondly, recent conversations with TVA reveal that some of the compounds that have been predicted are now known to have different structures. However for purposes of accounting and facility, the compounds were assumed to be correct. Perhaps this is why the predicted mass is always short of 1.0 lb. The water of hydration for some compounds could be modified. Further work in the area of crystal identification will add clarity to this problem. Is the precedence order correct or are there other elements besides fluorine that significantly affect the reaction process and therefore need to be incorporated into the model algorithm? How accurate are the in house elemental analyses? A variety of methods are used with the most difficult being those for aluminum and silicon. Aluminum analysis is performed on the AA and has an inherently weak signal to monitor. Silicon is presently being analyzed by a wet method which is of limited accuracy. Both of these elements play important and central roles in the model algorithm. The synergistic effects of combining the analyses for 30 wt% and 54 wt% P205 acid along with totlaizer data to obtain the starting levels for each impurity are significant. Finally, fluorine and silicon are lost from the acid as it moves through the process towards DAP but the amounts lost seem to be insignificant. The amount lost to process water and the atmosphere can be estimated and these values can be incorporated into the model.

Conclusion

The utility of the model does not lie solely with being able to estimate resultant grade from acid feed analyses. Quantitatively, there is some room for improvement, however on a qualitative level it will tell you about where grade will fall and provide some insight to the mechanism that will causes it. This in turn provides information on a regular basis that is needed for strategic decision making. Ex., at what level will we have to run the solid-liquid separators, and is it a single item that is

3 1 affecting grade or is it a combination of things? What are the options available to pursue? If elemental
2 1 analyses are well established the model will predict grade relatively well. It is the noise between acids
1 1 and DAP that must be better incorporated into the model and from there it is feasible that the model can be
3 extrapolated all the way back to rock. It is hoped that this information has stirred some interest in
developing a deterministic stance with respect to production.

References

1. Achorn, F. P., Salladay, D. G., Greenhill, J. L., and Dillard, E. F., "Effects of Process Parameters on Compositions of DAP Products", paper presented at the Fifth Annual TVA-TFI Phosphate Workshop, Atlanta, Georgia, February 19-20, 1980.
2. Achorn, F. P., E. F. Dillard, Frazier, A. W. and Salladay, D. G., "Effect of Impurities in Wet-Process Phosphoric Acids on DAP Grades", paper presented at the ISMA Conference, Vienna, Austria, November 11-13, 1980.
3. Achorn, F. P., E. F. Dillard, Frazier, A. W. and Woodis, T. C. Jr., "Precipitated Impurities in 18-46-0 Fertilizers Prepared from Wet-Process Phosphoric Acid", National Fertilizer Development Center, Tennessee Valley Authority, Bulletin Y-162, April 1981.
4. Hazeman, J. F., Lehr, J. R. and Smith, J. P., "Mineralogical Character of Iron and Aluminum Phosphates Containing Potassium and Ammonium", Soil Science Society of America Proceedings, V-15, pp 76-84, 1950.