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EFFECT OF IMPURITIES IN WET-PROCESS PHOSPHORIC ACIDS ON DAP GRADES

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This study is the result of cooperative work between commercial diammonium phosphate (DAP) producers, TVA field chemical engineers, and TVA Fundamental Research chemists. The purpose of the work was to discover the extent of grade control problems in the DAP industry and to offer some solutions to these problems. Field engineers visited several commercial plants and obtained operating data and samples. The engineers and chemists jointly evaluated these data. Table 1 shows analyses of several typical commercial DAP products. Fourteen samples were analyzed. Of this total, 29 percent did not meet the required 18-46-0 grade. Sources of phosphate rock for the DAP products were Central Florida, Northern Florida, North Carolina, and the western area.

Acids produced from these rocks have various impurity contents. TVA is hesitant to designate materials such as iron, aluminum, magnesium, calcium, and sulfur as impurities since some of these materials are excellent plant nutrients. However, for the purpose of this discussion it is assumed that they are impurities in phosphoric acid. Impurities considered were MgO , Fe_2O_3 , F , Al_2O_3 , CaO , and S . These impurities were totaled and plotted against the N content. Figure 1 shows a plot of total impurity versus N content. Generally, this plot shows that as the total impurity content increases, the amount of N decreases. Figure 2 shows the same result for P_2O_5 ; namely, as the total impurity content increases, the P_2O_5 content decreases.

Further investigation showed that some companies were still able to produce the required grade at high impurity contents. Additional investigations showed that although the total impurity content is an important factor in on-grade

production, a reduction in grade can be minimized if the impurities are combined with a maximum amount of N and citrate soluble P_2O_5 and a minimum of water. A primary purpose of the investigation was to determine operating procedures that will allow a maximum combination of N and citrate soluble P_2O_5 with the impurities present in the product. Also, it is desirable that the N and P_2O_5 be combined with the impurity at or near the N: P_2O_5 weight ratio of DAP (0.39:1).

In TVA's work with one company that uses Central Florida phosphate rock for production of phosphoric acid, it was assumed that impurities in the product had a high content of combined water or water of hydration (molecular water), which caused a decrease in the total grade of the product. Further investigations showed that this assumption was not entirely correct. The total water content (water of hydration + free water) does affect the total plant nutrient content as would normally be expected; the water acts as a diluent and helps decrease the N and P_2O_5 contents of the grade. Figure 3 shows a plot of total water content versus N content of the grade. This plot shows that, generally, the higher the total water content, the lower the N content. Figure 4 shows that there is a more dramatic decrease in the P_2O_5 content as the total water content increases.

However, when an attempt was made to plot the molecular water content versus the N and P_2O_5 contents of the product, no conclusion could be made concerning the relationship between water content and total N or P_2O_5 contents. Figures 5 and 6 indicate that there is a general trend for the N and P_2O_5 content to decrease as the combined water increases. Additional microscopic analyses confirmed these results and showed that the molecular water content of the impurities was not one of the major causes for low N and/or P_2O_5 content.

Calcium Problems

Further investigations at other DAP plants showed that acids with high Ca contents usually resulted in products with low N contents (figure 7). Obviously, Ca in the acid combined with some of the P_2O_5 to produce calcium phosphates thus leaving less P_2O_5 available for ammoniation. The Ca also has a diluent effect on the grade. Investigations at several phosphoric acid plants showed that the acids contain higher Ca contents for several reasons, two of which are:

1. Operation of the phosphoric acid unit at high extraction temperatures which causes an unusually large amount of Ca as $CaSO_4$ to be dissolved in the product acid from the plant.
2. The type of filter used, maintenance of the filter cloth, or the type of filter cloth used.

Obviously, the amount of Ca can be decreased by clarification. However, this process is expensive and most producers prefer to minimize the amount of clarification conducted in their plants.

Generally, the analytical data show that when the CaO content of the product DAP was decreased to less than 0.6 percent, grade problems were easier to rectify in the plants.

Iron Problems

The CaO content is not the only cause for low-grade DAP. Other impurities also cause problems. Figure 8 shows a plot of R_2O_3 ($Al_2O_3 + Fe_2O_3$) versus N content of the DAP samples. Generally as the R_2O_3 content increased, nitrogen content decreased. Other data show a different result for P_2O_5 in that increased R_2O_3 content did not seem to have a great effect on the P_2O_5 content of the product; however, the results are erratic. Frazier has reported that F and SO_3 contents do have a significant effect on P_2O_5 content (1) (2). He has reported that sometimes a citrate-insoluble (C.I.) $FeNH_4(HPO_4)_2$ forms.

Operating data were obtained from the plants that provided the DAP samples (table 1). This data along with some analytical results are shown in table 2. These data show that for products containing low F concentrations (<2% F) retention time in the preneutralizer affects the amount of C.I. P_2O_5 in the product. These data show that as the retention time in the preneutralizer is increased, C.I. P_2O_5 in the product also increases. Frazier reported that this increased C.I. P_2O_5 is caused by formation of relatively large-sized crystals of $FeNH_4(HPO_4)_2$. Obviously, the preferable way to lower retention time in the preneutralizer is to decrease the effective size of this tank. This can be accomplished by one of the following:

1. Lower depth of slurry in the existing preneutralizer.
2. Install a smaller preneutralizer.
3. Install a pipe-cross or pipe reactor.

Some operators fear they will encounter high ammonia losses and low evaporation of water from the preneutralizer if retention time is decreased. If this is a problem, it might be preferable to install two preneutralizers as shown in the flow diagram of figure 9. This is the flow diagram used by company F (table 2). The first preneutralizer is relatively large and is operated at an N:P mole ratio of 0.6:1. Microscopic and chemical analyses show that at this low degree of ammoniation there is no reversion of P_2O_5 to an unavailable form. Exit gases from this preneutralizer may contain fluorine; however, the gases will not contain NH_3 . Because of the large exposed surface area of slurry in the first preneutralizer, there is excellent evaporation efficiency. The degree of ammoniation in the second preneutralizer results in

a slurry having an N:P mole ratio of 1.4:1 to 1.5:1. Frazier reports that C.I. $\text{FeNH}_4(\text{HPO}_4)_2$ forms at the higher degrees of ammoniation (1). Since retention time in this preneutralizer is low, $\text{FeNH}_4(\text{HPO}_4)_2$ crystallizes as small crystals having available P_2O_5 .

These analytical results were compared with plant data obtained from company F (table 2). Total retention time in this company's two preneutralizers is relatively high (135 minutes); retention time in the second preneutralizer, in which the N:P mole ratio of the slurry is 1.45:1, is low (28 minutes). The C.I. P_2O_5 in this company's product is relatively low as compared with the C.I. P_2O_5 in the products of some of the other companies which also had relatively high slurry retention time in their single preneutralizers.

One company operated a preneutralizer in combination with a pipe-cross reactor or pipe reactor slightly different from the design shown in figure 10. The design shown in figure 10 is that used in the TVA pilot plant for production of DAP and it is TVA's recommended design for large plants. This is a reactor with a very short slurry retention time. It is made of standard Hastelloy C 276 pipe fittings and can be operated as the only preneutralizer or in combination with a first stage preneutralizer which would operate at a low N:P mole ratio (0.6:1). Slurry from the pipe-cross reactor should have an N:P mole ratio of 1.4:1 to 1.5:1. Commercial and pilot plant tests show that this reactor can be successfully used to produce either diammonium phosphate (DAP) or monoammonium phosphate (MAP) or ammonium phosphate sulfate (APS).

Importance of Fluorine

The operating and analytical data in table 2 for products with fluorine contents in excess of 2% show that retention time in the preneutralizer has little or no effect on citrate solubility of P_2O_5 in the product. Analytical data show that when there is insufficient F in the product to combine with the

Fe, C.I. $\text{FeNH}_4(\text{HPO}_4)_2$ forms; operating data confirm these analytical results. These data show that as the F: Fe_2O_3 wt ratio increases, the C.I. P_2O_5 decreases; at an F: Fe_2O_3 wt ratio of 2.3:1, the C.I. P_2O_5 is less than 0.1%. These data suggest that F as ammonium fluoride (NH_4F) should be added or returned to the preneutralizers. In a two-stage preneutralizer operation this NH_4F could be obtained by scrubbing the exit gases of the first stage preneutralizer with some of the ammonia-containing exit gas from the ammoniator. This NH_4F could then be returned to the second stage preneutralizer. At the N:P mole ratio in the slurry from the second preneutralizer there is essentially no loss of fluorine.

Effect of Slurry Temperature

Data in table 2 also show that the temperature of the slurry from the preneutralizer or granulator seems to have little effect on the content of C.I. P_2O_5 in the product provided product temperatures from the ammoniation units are less than 250°F for the preneutralizers and 210°F for the ammoniator-granulator. Additional data are needed to determine if there is an upper temperature limit for ammoniation.

Effect of Magnesium

Many phosphate rocks now available in the U.S. have higher magnesium contents than were common in the recent past. Some U.S. DAP producers have expressed concern that it will be difficult to make DAP grade with phosphoric acid produced from these rocks. Pilot-plant and commercial-scale-plant tests show that magnesium content of the acid has much less diluent effect than either calcium or iron content in the acid (3) (4) (5). There is not complete agreement as to the chemical composition of the magnesium compound in DAP; however, TVA's latest

microscopic examinations indicate it to be $MgNH_4PO_4 \cdot H_2O$. This compound does not have the diluent effect of compounds containing Ca and Fe because its molecular weight is much less than the other diluents and because the magnesium is combined with both N and P.

It has also been assumed by some operators that magnesium is the cause for high viscosities in preneutralizer slurries. At TVA two samples of DAP were analyzed both chemically and microscopically. One sample (IMC-1) contained only 0.38% magnesium and the other (IMC-2) contained 0.71%. These samples were obtained from products produced in TVA's pilot plant. This pilot plant is similar to the sketch of the commercial plant shown in figure 9 except that the pilot plant has much smaller equipment and only one preneutralizer is used. Its capacity is 0.5 ton per hour. A summary of some operating and chemical data for the two tests in which these products were produced is shown in table 3. The microscopic and chemical data of a DAP product that has a relatively low Mg content (IMC-1) are shown in table 4 and the same type of data for a DAP product that has a higher Mg content (IMC-2) is shown in table 5. Data in these tables show that within the range of these tests magnesium seems to have little or no effect on viscosity of the preneutralizer slurry, operation of the plant, or product quality.

Microscopic results show that when the F:Fe₂O₃ wt ratio in the phosphoric acid feed is low (about 1:1) larger quantities (about 4.2%) of Fe-NH₄-PO₄-NH₂O form in the product than when an acid with a higher F:Fe₂O₃ wt ratio (about 2:1) is used. Microscopic data also show the Fe-NH₄-PO₄-NH₂O solid phase is of small colloidal size, which results in formation of colloidal gels in the slurry. Increased amounts of colloidal gels in preneutralizer slurry are one reason for increased slurry viscosity. The summary of these results is tabulated below:

<u>Test No.</u>	<u>H₃PO₄ Feed F:Fe₂O₃ Wt Ratio</u>	<u>DAP Product Percent by Weight Fe-NH₄-PO₄-NH₂O</u>	<u>Preneutralizer Slurry Viscosity, cP</u>
IMC 1	1.02:1	4.2	466
IMC 2	2.17:1	0.96	166

When larger quantities of F are present in the slurry, a coarser compound such as Fe-NH₄-PO₄-F-H₂O is usually formed and higher slurry viscosities are avoided. Therefore, it is concluded that Mg is not the contributing factor for high viscosities in the preneutralizer and that formation of the Fe precipitate is the most important factor. The Fe-NH₄-PO₄-NH₂O forms in colloidal size when retention time in the preneutralizer is low. Therefore, to realize the benefits of low retention time (low C.I.-P₂O₅ in product) and to avoid pumping problems with highly viscous slurries, it is advisable that a pipe reactor be used to produce DAP. When this equipment (figure 10) is used, retention time during preneutralization is low and highly viscous slurries can be sprayed onto the bed of material in the granulator. In this way maximum availability of P₂O₅ can be obtained and the difficulty of pumping highly viscous slurries can be avoided.

Summary of all Significant Chemical Compounds in DAP

Table 6 shows the calculated percentages of each compound in a DAP sample which was on-grade (18.2-46.2-0). Table 7 shows these same percentages for a DAP sample that was off-grade (18.0-45.6-0). Note the relatively large amount (5.95 percent) of FeNH₄(HPO₄)₂ in the off-grade product. Because this compound was precipitated as large crystals, it had a detrimental effect on the P₂O₅ of the grade. Also note the relatively large quantity (4.2 percent) of calcium ammonium phosphate, Ca(NH₄)₂(HPO₄)₂·H₂O, in the off-grade product. There was a small amount (1.86 percent) of this diluent in the on-grade product. This diluent

as well as the diluent effect of the 6.6 percent of ammonium sulfate was at least partially caused by the high gypsum content in the acid used to manufacture the DAP.

Summary

Results of this study identify the main problems in meeting DAP grade specifications and suggest some possible solutions to these problems as follows:

1. The major source of grade deficiency in the commercial samples which were investigated was calcium. Some solutions to this problem are to maintain filter cloths in the phosphoric acid unit in good condition, operate the phosphoric acid unit at as low an acid temperature as consistent with good operation of this unit, and partially clarify the acid before it is used.
2. In the DAP unit the amount of Fe_2O_3 and F in the acid affects the content of C.I. P_2O_5 in the product. If the F: Fe_2O_3 wt ratio in the product can be kept above 2.3:1, probably the C.I.- P_2O_5 content of the product will be less than 0.1 percent. At lower F: Fe_2O_3 wt ratios, it is advantageous to have low retention times in the preneutralizer and ammoniator-granulator when the N:P mole ratio is 1.4:1 or higher.
3. Other data show that the N:P mole ratio in the slurry from the preneutralizer to the granulator must be above 1.4:1 to avoid nitrogen deficiencies. At lower ratios the product will contain some MAP; this causes nitrogen deficiency in the products.
4. The Mg and Al contents of the acids have less effect on grade deficiency than Ca and Fe.
5. To avoid highly viscous preneutralizer slurries when low preneutralizer retention times are used, ensure that there is sufficient F available (F: Fe_2O_3 wt ratio >2.0:1) to combine with the Fe_2O_3 to form coarse crystals.

An alternative to this latter suggestion is to replace the preneutralizer with a TVA pipe reactor which is partially installed in the granulator and discharges viscous slurry directly onto the bed of material in the granulator.

References

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Table 1

Chemical Analysis of Commercial DAP
Weight Percent

Sample	Total N	P ₂ O ₅		Total Fe ₂ O ₃	Total Al ₂ O ₃	Total MgO	H ₂ O			Total F	Total CaO	Total S	Total MgO, Fe ₂ O ₃ F, Al ₂ O ₃ , CaO, S
		Total	C.I.				Total	Free	Combined				
A	18.3	46.5	0.07	1.6	1.3	0.69	2.5	1.8	0.7	2.6	0.44	1.3	7.93
B	18.2	46.2	0.05	1.7	1.3	0.71	2.9	2.1	0.8	2.4	0.46	1.4	7.97
C	18.3	46.5	0.37	1.8	1.2	0.62	1.9	1.7	0.2	1.2	0.29	2.0	7.11
D	18.0	46.0	0.32	2.0	1.3	0.79	3.0	2.0	1.0	2.4	0.57	1.3	8.36
E	18.0	46.2	0.18	1.7	1.2	0.61	2.8	2.3	0.5	1.8	0.56	1.7	7.57
F	18.2	46.6	0.04	1.9	1.2	0.72	2.6	2.2	0.4	1.5	0.42	1.6	7.34
G	18.3	47.3	0.84	1.7	1.1	0.58	1.7	1.4	0.3	1.7	0.40	1.4	6.88
H	18.2	46.8	0.01	1.8	1.2	0.57	2.4	1.7	0.7	1.4	0.46	1.8	7.23
I	18.7	45.3	0.08	1.1	1.4	0.55	2.6	1.9	0.7	2.5	0.43	1.7	7.68
J	18.7	47.4	Nil	0.67	0.48	0.70	1.8	1.2	0.6	1.4	1.30	1.7	6.25
K	18.6	47.4	Nil	0.67	0.48	0.69	1.7	1.2	0.5	1.4	1.30	1.7	6.24
L	17.1	44.8	0.10	0.86	1.7	0.63	3.1	2.3	0.8	3.2	1.80	1.7	9.89
M	17.2	46.7	0.46	1.57	2.1	0.71	3.7	2.8	0.9	1.7	0.69	1.4	8.17
N	17.9	45.2	0.01	1.50	1.6	0.55	3.3	2.7	0.6	2.7	0.76	1.6	8.71

Table 2

Effect of Preneutralizer Retention Time on Citrate
Insoluble P₂O₅ in DAP

Sample	No. of Preneutralizers	Total Retention Time in Preneutralizer (min)	Citrate- Insoluble P ₂ O ₅ (%)	Temperatures, °C (°F)		Fe ₂ O ₃ (%)	F (%)	Al ₂ O ₃ (%)	F:Fe ₂ O ₃ Wt Ratio
				Slurry to Granulator	Product from Granulator				
Products of low F content (<2%)									
A	1	31	Nil	113(235)	99(210)	1.9	1.5	1.2	0.79:1
B	1	48	Nil	118(245)	96(205)	0.67	1.4	0.48	2.1:1
C	1	49	0.1	111(232)	92(197)	1.8	1.4	1.2	0.78:1
D	1	61	0.18	121(250)	96(205)	1.7	1.8	1.2	1.06:1
E	1	98	0.84	110(230)	79(175)	1.7	1.7	1.1	1.0:1
F	2	135 ^a	0.37	116(240)	85(185)	1.8	1.2	1.2	0.67:1
Products with relatively high F content (>2%)									
G	1	74	0.32	107(225)	96(204)	2.0	2.4	1.3	1.20:1
H	1	83	0.08	117(242)	93(200)	1.1	2.5	1.4	2.27:1
I	1	128	0.27	116(240)	99(210)	1.7	2.6	1.6	1.53:1

^aRetention time 1st preneutralizer 107 min, 2nd preneutralizer 28 min
N:P mole ratio 1st preneutralizer = 1.15:1, 2nd preneutralizer 1.5:1.

Table 3

Pilot Plant Production DAP - Effect of Magnesium

<u>Phosphoric Acid Analysis, %</u>	<u>Test No.</u>	
	<u>IMC-1^a</u>	<u>IMC-2^b</u>
MgO	0.56	1.63
P ₂ O ₅	40.59	40.03
F	2.05	2.46
Fe ₂ O ₃	2.01	1.13
Al ₂ O ₃	1.09	1.41
CaO	0.06	0.32
SO ₃	2.36	2.80
SiO ₂	-	1.09
<u>Ratios</u>		
F:Fe ₂ O ₃	1.02:1	2.17:1
F:MgO	3.66:1	1.51:1
F:R ₂ O ₃	0.66:1	0.97:1
<u>Preneutralizer Slurry Operating Data</u>		
Temperature, °C (°F)	109(229)	107(224)
Viscosity, cP	466	152
Specific gravity	1.42	1.44
pH	6.3	6.3
N:P mole ratio	1.46:1	1.37:1
<u>Slurry Chemical Analysis, %</u>		
N	10.6	9.9
P ₂ O ₅	36.8	36.7
H ₂ O (A.O.A.C.)	29.1	29.0

^aCombination 3 tests: NW-1, 2, 3

^bCombination 4 tests: NW-6, 7, 8, 9

Table 4

Microscopic and Chemical Analysis of DAP Product Having Low Magnesium Content, Weight Percent

Test No. IMC-1
C.I. P₂O₅ = 0.05 Percent
Slurry Viscosity 466 cP

Solid	WT %	F	Ca	N	P ₂ O ₅	Fe	Al	Mg	SO ₄	Zn	V	Cr	Cd	U	Ni	Mn	Si	Na	K
MgNH ₄ PO ₄ ·H ₂ O	2.11			0.19	0.96			0.33											
Ca ₄ SO ₄ AlSiF ₁₃ ·12H ₂ O	0.30	0.095	0.06				0.01		0.04										
ZnNH ₄ PO ₄	0.025			0.002	0.010					0.0092									
CdNH ₄ PO ₄	0.002			0.0001	0.001								0.0010						
UO ₂ NH ₄ PO ₄	0.028			0.001	0.006									0.0190					
NiNH ₄ PO ₄	0.007			0.0006	0.003										0.0024				
MnNH ₄ PO ₄	0.083			0.007	0.035											0.0271			
NaH ₂ PO ₄	0.20				0.024													0.0383	
KH ₂ PO ₄	0.14																		0.0408
Al-NH ₄ -PO ₄ -F-H ₂ O	4.44	0.94		0.35	1.76		0.67												
Fe-NH ₄ -PO ₄ -NH ₂ O	4.90			0.23	1.94	1.22													
Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	0.36		0.05	0.035	0.18														
V-NH ₄ -PO ₄ -F-H ₂ O	0.05	0.009		0.003	0.017						0.0126								
Cr-NH ₄ -PO ₄ -F-H ₂ O	0.03	0.006		0.002	0.01							0.0076							
(NH ₄) ₂ SiF ₆	1.16	0.74		0.21													0.21		
(NH ₄) ₂ SO ₄	6.24			1.32					4.54										
NH ₄ H ₂ PO ₄	6.74			0.82	4.16														
(NH ₄) ₂ HPO ₄	72.65			15.41	39.08														
Free H ₂ O	0.68																		
Summation	100.14	1.79	0.11	18.58	48.19	1.22	0.68	0.33	4.58	0.0092	0.0126	0.0076	0.0010	0.0190	0.0024	0.0271	0.21	0.0383	0.0408
Chemical analysis	-	1.79	0.11	18.58	48.19	1.22	0.68	0.33	4.58	0.0093	0.0125	0.0080	0.0008	0.0187	0.0024	0.0273	0.14	0.0390	0.0408

Table 5

Microscopic and Chemical Analysis of DAP Product Having High Magnesium Content, Weight Percent

Test No. IMC-2
 C.I. P₂O₅ = 0.37 Percent
 Slurry Viscosity 166 cP

Solid	WT %	F	Ca	N	P ₂ O ₅	Fe	Al	Mg	SO ₄	Zn	V	Cr	Cd	U	Ni	Mn	Si	Na	K
MgNH ₄ PO ₄ ·H ₂ O	4.15			0.37	1.90			0.65											
Ca ₄ SO ₄ AlSiF ₁₃ ·12H ₂ O	0.05	0.02	0.01				0.002		0.006								0.0018		
ZnNH ₄ PO ₄	0.018			0.001	0.007					0.0066									
CdNH ₄ PO ₄	0.001			0.0001	0.0003								0.0005						
UO ₂ NH ₄ PO ₄	0.030			0.001	0.006									0.0203					
NiNH ₄ PO ₄	0.005			0.0004	0.002										0.0017				
MnNH ₄ PO ₄	0.09			0.008	0.038											0.0294			
NaH ₂ PO ₄	0.16				0.095													0.0307	
Fe ₃ KH ₄ (PO ₄) ₈ ·4H ₂ O	0.96				0.52	0.15													0.0356
Fe-NH ₄ -PO ₄ -NH ₂ O	0.28			0.01	0.11	0.07													
Fe-NH ₄ -PO ₄ -F-H ₂ O	3.59	0.66		0.24	1.23	0.97													
Al-NH ₄ -PO ₄ -F-H ₂ O	4.51	0.96		0.35	1.79		0.68												
V-NH ₄ -PO ₄ -F-H ₂ O	0.05	0.009		0.003	0.017						0.0126								
Cr-NH ₄ -PO ₄ -F-H ₂ O	0.03	0.006		0.002	0.01							0.0076							
Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	0.36		0.05	0.04	0.18														
(NH ₄) ₂ SiF ₆	0.91	0.58		0.14													0.143		
(NH ₄) ₂ SO ₄	3.88			0.82					2.82										
(NH ₄) ₂ HPO ₄	75.81			16.08	40.78														
(NH ₄) ₃ PO ₄	2.17			0.59	0.97														
Free H ₂ O	1.06																		
Summation	98.11	2.24	0.06	18.66	47.66	1.19	0.682	0.65	2.826	0.0066	0.0126	0.0076	0.0005	0.0203	0.0017	0.0294	0.1438	0.0307	0.0356
Chemical analysis	-	2.24	0.06	18.66	47.66	1.19	0.68	0.65	2.83	0.0067	0.0127	0.0066	0.0006	0.0204	0.0018	0.0293	0.2165	0.0311	0.0356

Table 6
Microscopic and Chemical Analysis of On-Grade DAP (18.2-46.2-0), Weight Percent

Solid	Wt %	F	Ca	N	P ₂ O ₅	Fe	Al	Mg	SO ₄	Zn	V	Mn	Cr	Cd	U	Ni	Si
MgNH ₄ PO ₄ · H ₂ O	2.92			0.25	1.25			0.43									0.01
Ca ₄ SO ₄ AlSiF ₁₃ · 12H ₂ O	0.36	0.11	0.07				0.01		0.04								
ZnNH ₄ PO ₄	0.02			0.002	0.008					0.0073							
CdNH ₄ PO ₄	0.0004			0.00002	0.0002									0.0002			
UO ₂ NH ₄ PO ₄	0.03			0.001	0.006										0.02		
NiNH ₄ PO ₄	0.005			0.0004	0.002											0.002	
MnNH ₄ PO ₄	0.11			0.009	0.047							0.036					
FeNH ₄ (HPO ₄) ₂	0.84			0.04	0.43	0.17											
Fe-NH ₄ -PO ₄ -F-H ₂ O	3.78	0.69		0.25	1.29	1.02											
Al-NH ₄ -PO ₄ -F-H ₂ O	4.44	0.94		0.35	1.76		0.67										
V-NH ₄ -PO ₄ -F-H ₂ O	0.06	0.01		0.004	0.021						0.015						
Cr-NH ₄ -PO ₄ -F-H ₂ O	0.03	0.006		0.002	0.01								0.0076				
Ca(NH ₄) ₂ (HPO ₄) ₂ · H ₂ O	1.86		0.26	0.18	0.92												
(NH ₄) ₂ SIF ₆	1.08	0.69		0.17													0.17
(NH ₄) ₂ SO ₄	5.71			1.21					4.15								
(NH ₄) ₂ HPO ₄	73.1			15.5	39.32												
NH ₄ H ₂ PO ₄	1.85			0.23	1.14												
Free H ₂ O	2.1																
Summation	98.3	2.45	0.33	18.2	46.2	1.19	0.688	0.43	4.19	0.0073	0.015	0.036	0.0076	0.0002	0.02	0.002	0.18
Chemical analysis		2.4	0.33	18.2	46.2	1.19	0.69	0.43	4.19	0.0077	0.0147	0.0369	0.0077	0.0002	0.0183	0.0017	-

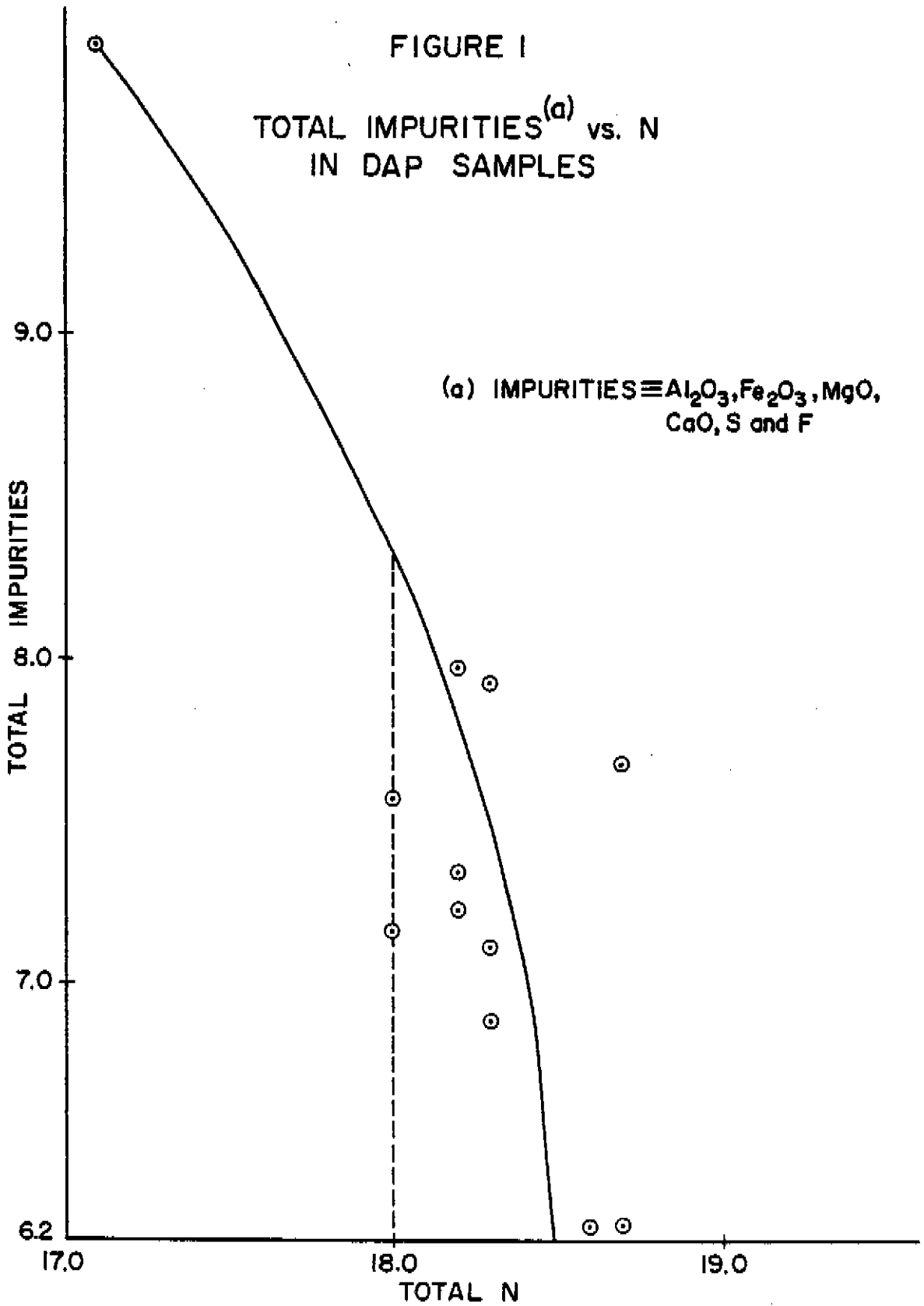
Table 7

Microscopic and Chemical Analysis of Off-Grade DAP (18.0-45.6-0), Weight Percent

Solid	WT %	F	Ca	N	P ₂ O ₅	Fe	Al	Mg	SO ₄	Zn	V	Cr	Cd	U	Ni	Mn
MgNH ₄ PO ₄ ·6H ₂ O	2.66			0.22	1.14			0.39								
Ca ₄ SO ₄ AlSiF ₁₃ ·12H ₂ O	0.72	0.23	0.15				0.02		0.09							
ZnNH ₄ PO ₄	0.01			0.001	0.004					0.004						
CdNH ₄ PO ₄	0.001			0.0001	0.0003								0.0005			
UO ₂ NH ₄ PO ₄	0.03			0.001	0.006									0.020		
NiNH ₄ PO ₄	0.004			0.0003	0.002										0.001	
MnNH ₄ PO ₄	0.09			0.008	0.038											0.029
FeNH ₄ (HPO ₄) ₂	5.95			0.30	3.07	1.21										
Al-NH ₄ -PO ₄ -F-H ₂ O	4.71	1.00		0.37	1.87		0.71									
V-NH ₄ -PO ₄ -F-H ₂ O	0.06	0.01		0.004	0.021						0.015					
Cr-NH ₄ -PO ₄ -F-H ₂ O	0.02	0.004		0.001	0.007							0.005				
Ca(NH ₄) ₂ (HPO ₄) ₂ ·H ₂ O	4.22		0.59	0.41	2.10											
(NH ₄) ₂ SiF ₆	0.78	0.50		0.12												
(NH ₄) ₂ SO ₄	6.59			1.40					4.79							
(NH ₄) ₂ HPO ₄	66.08			14.02	35.54											
(NH ₄) ₃ PO ₄	4.20			1.15	1.88											
Free H ₂ O	2.7															
Summation	98.8	1.74	0.74	18.01	45.67	1.21	0.73	0.39	4.88	0.004	0.015	0.005	0.0005	0.020	0.002	0.029
Chemical analysis		1.8	0.74	18.00	45.67	1.21	0.71	0.39	4.79	0.0043	0.0140	0.0055	0.0006	0.0199	0.0014	0.0283

FIGURE I

TOTAL IMPURITIES^(a) vs. N
IN DAP SAMPLES



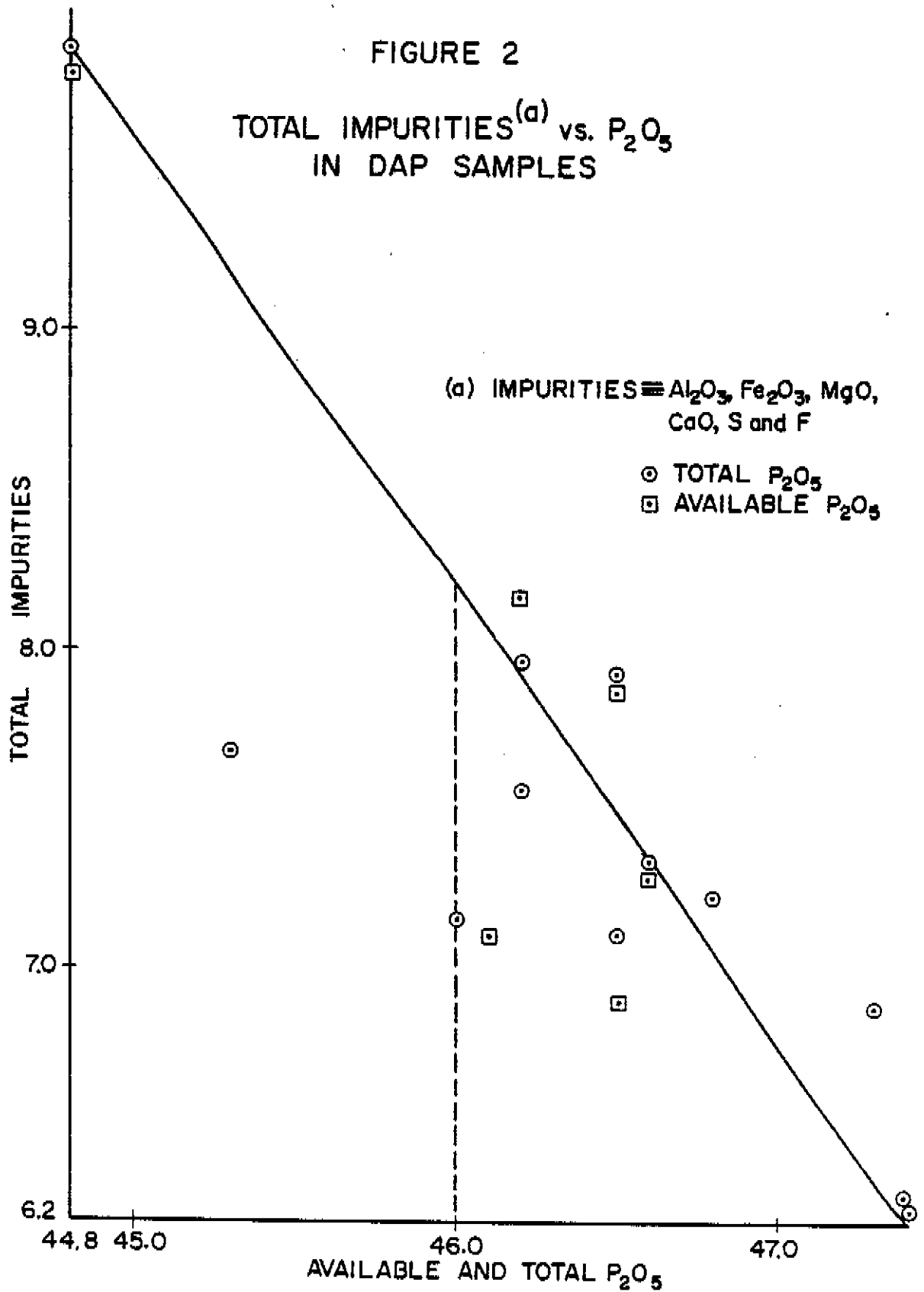


FIGURE 3

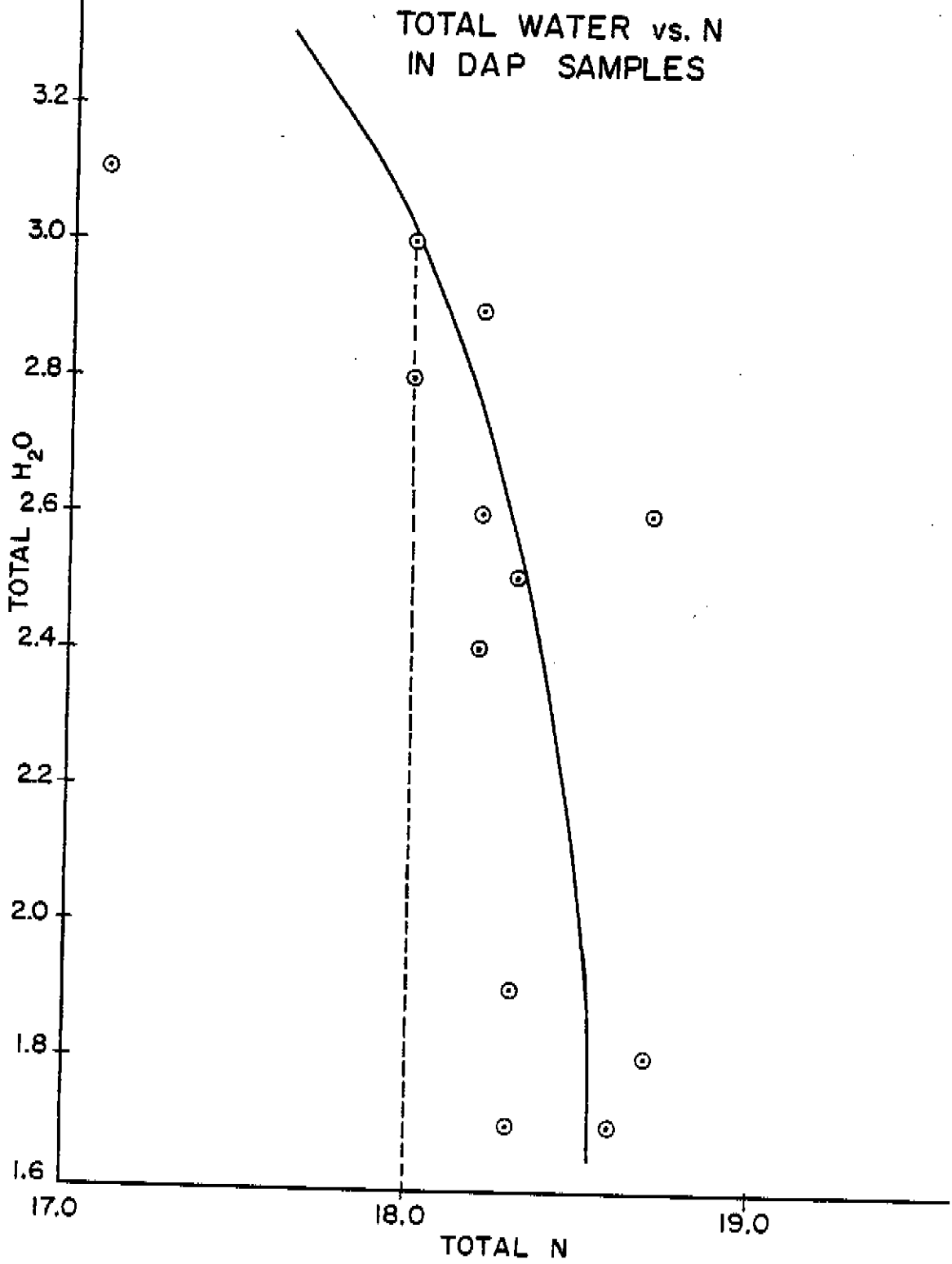


FIGURE 4

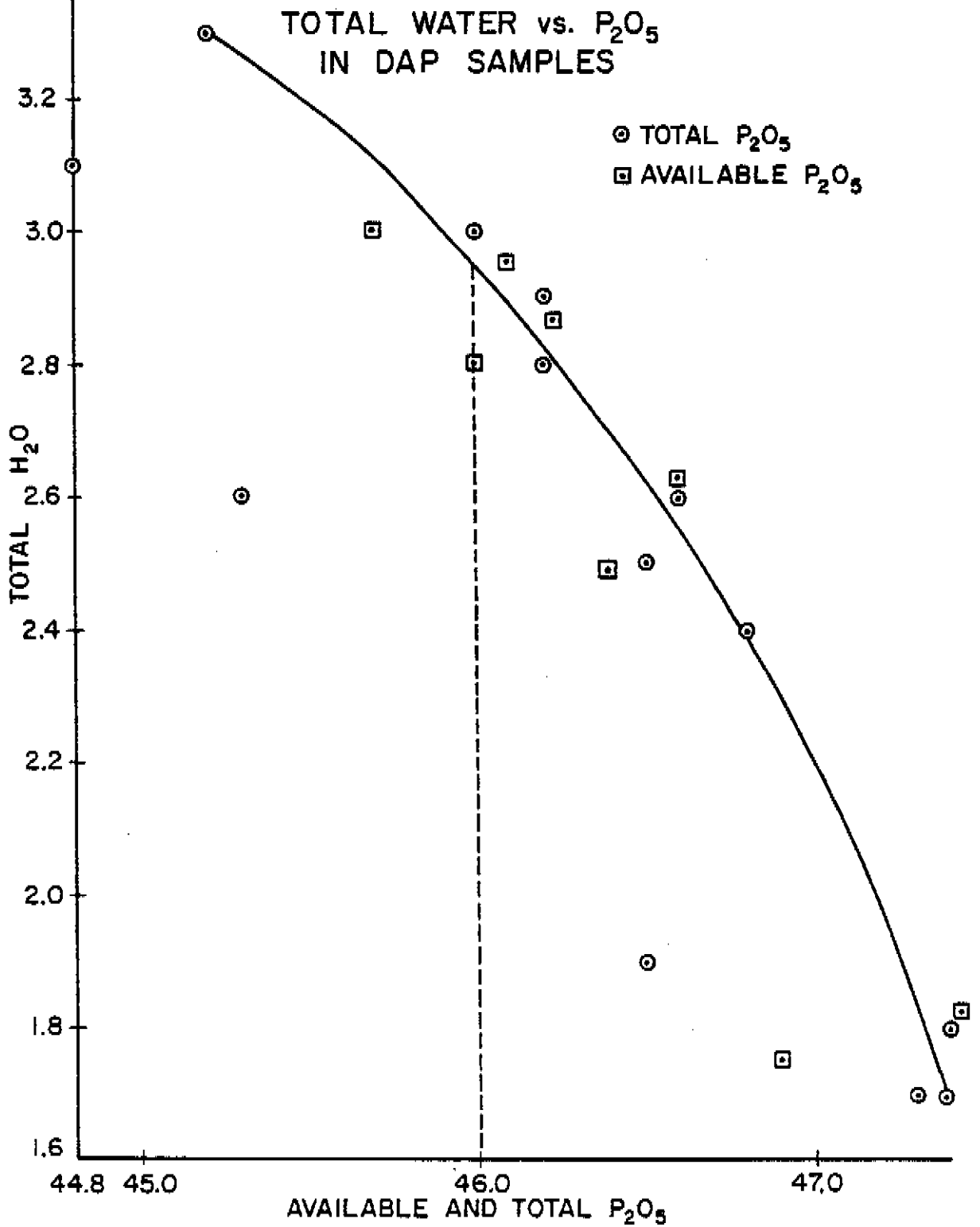


FIGURE 5
COMBINED WATER vs. N
IN DAP SAMPLES

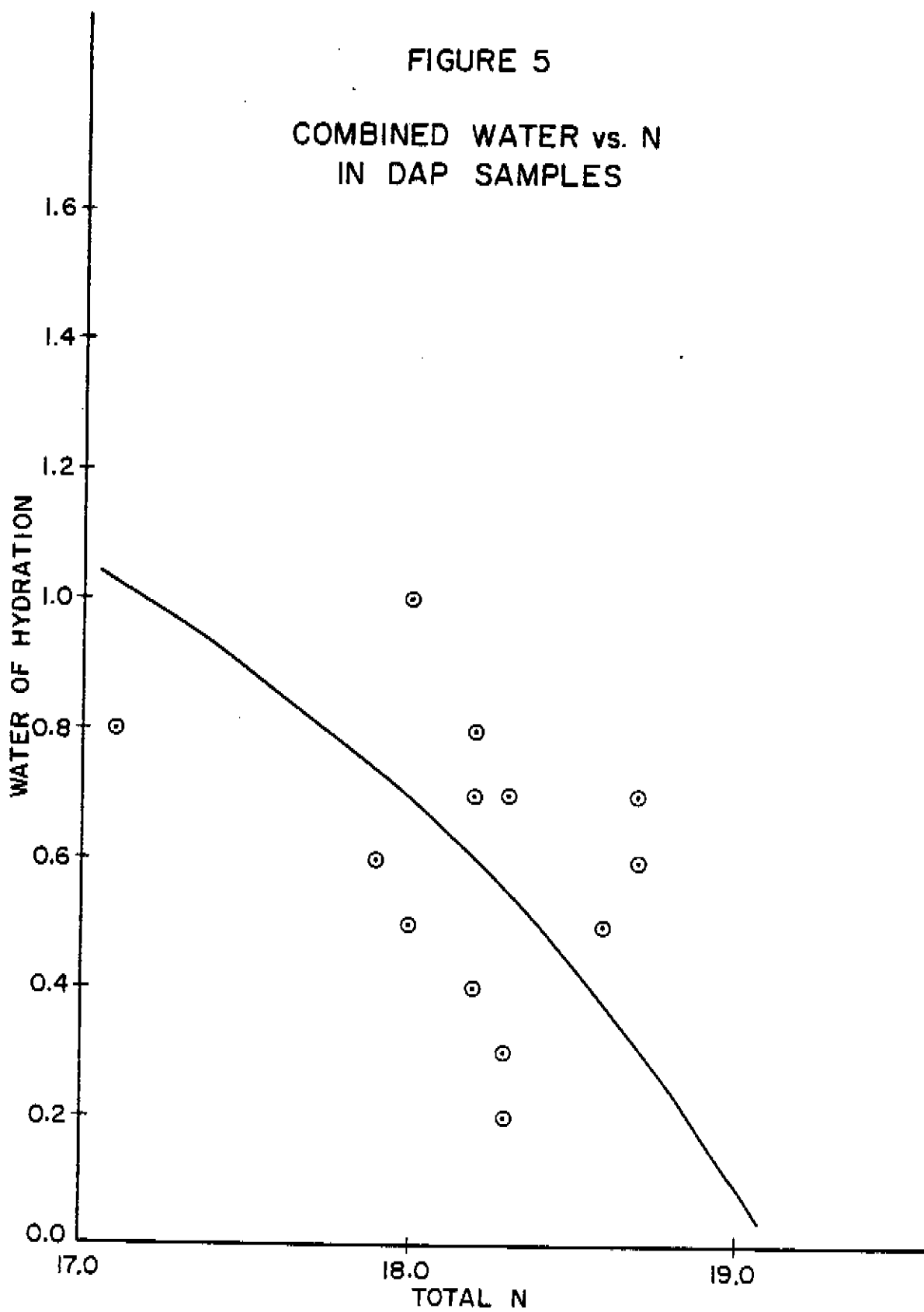


FIGURE 6

COMBINED WATER vs. P_2O_5
IN DAP SAMPLES

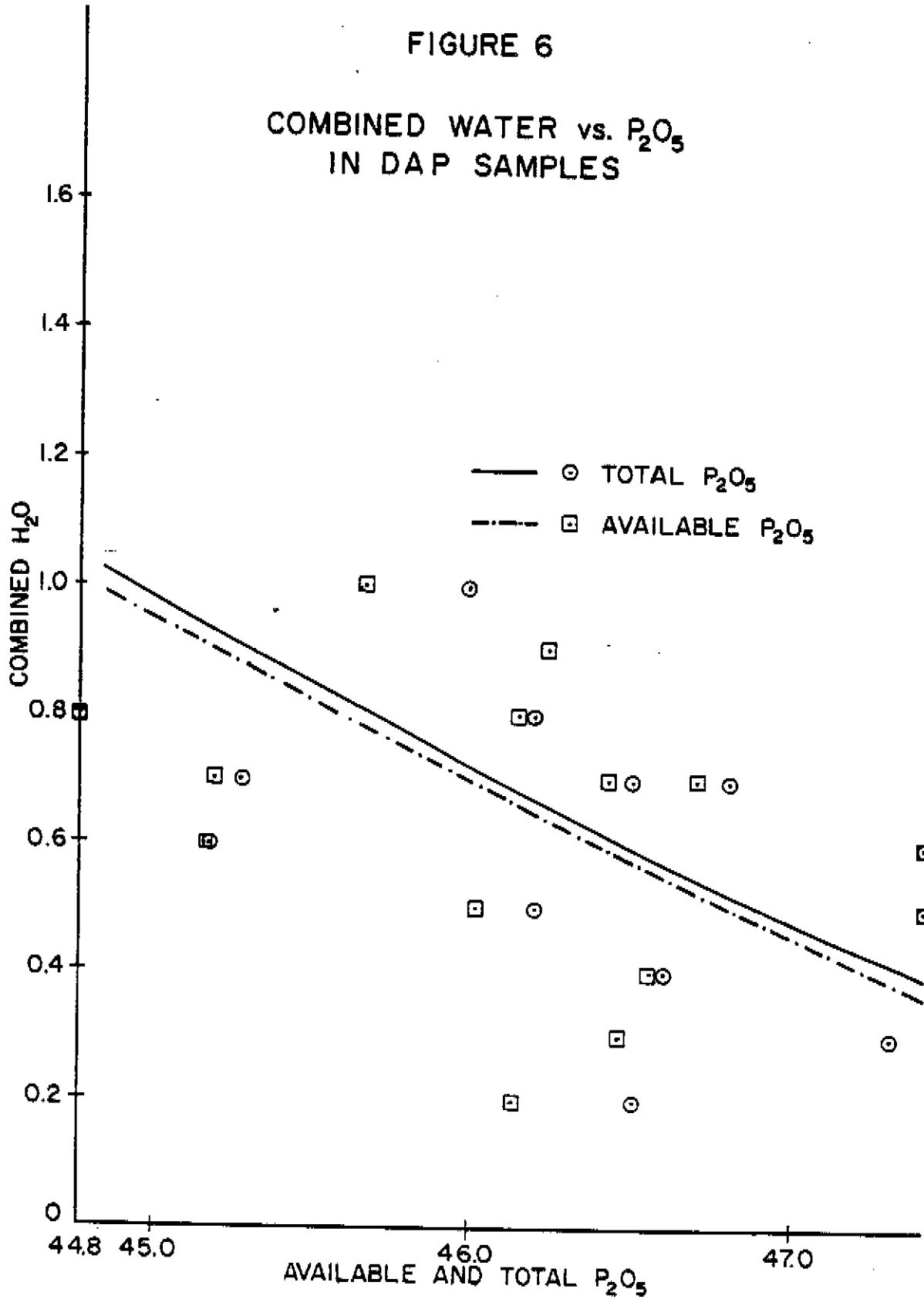


FIGURE 7

TOTAL CaO vs. N
IN DAP SAMPLES

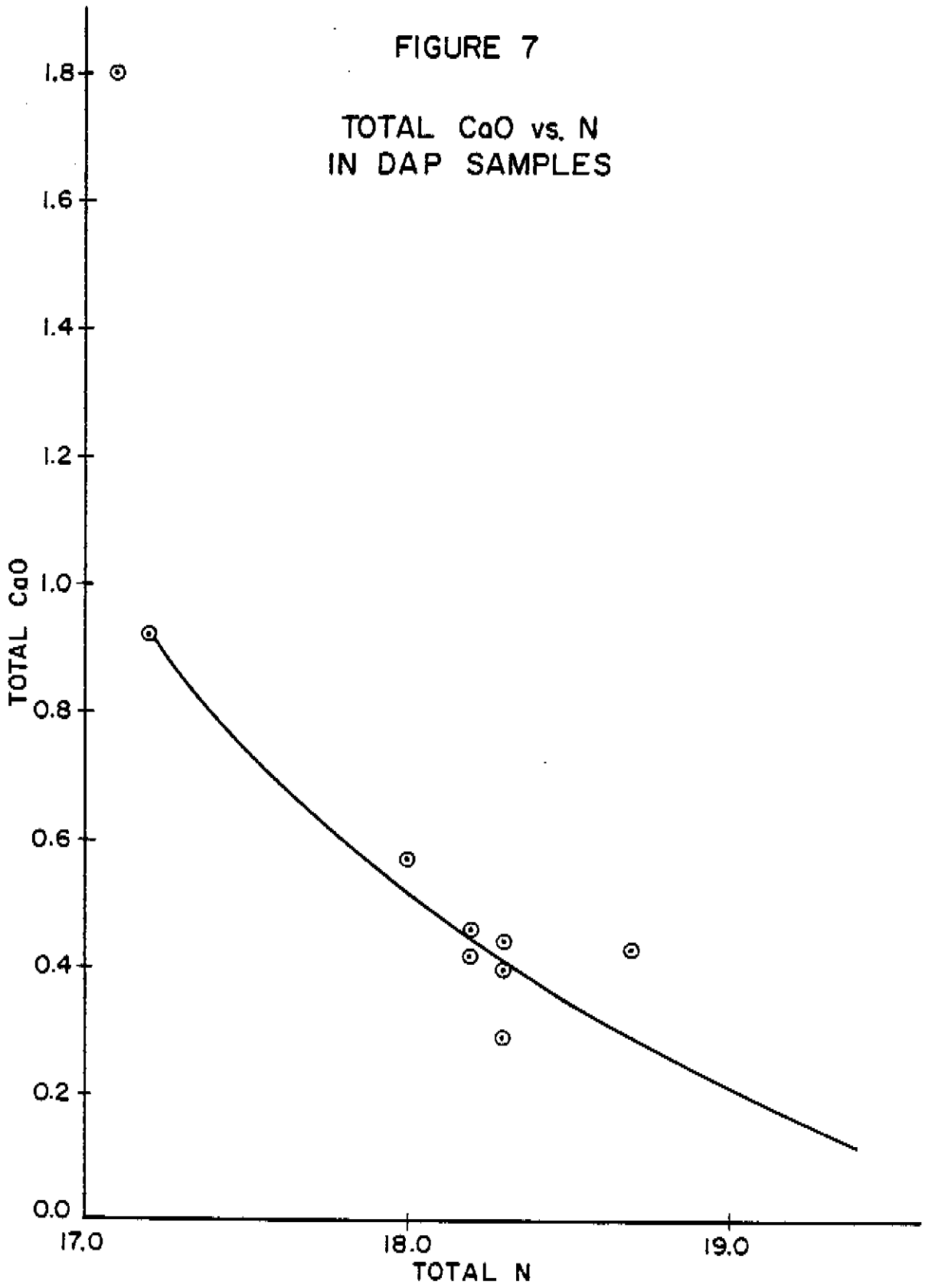
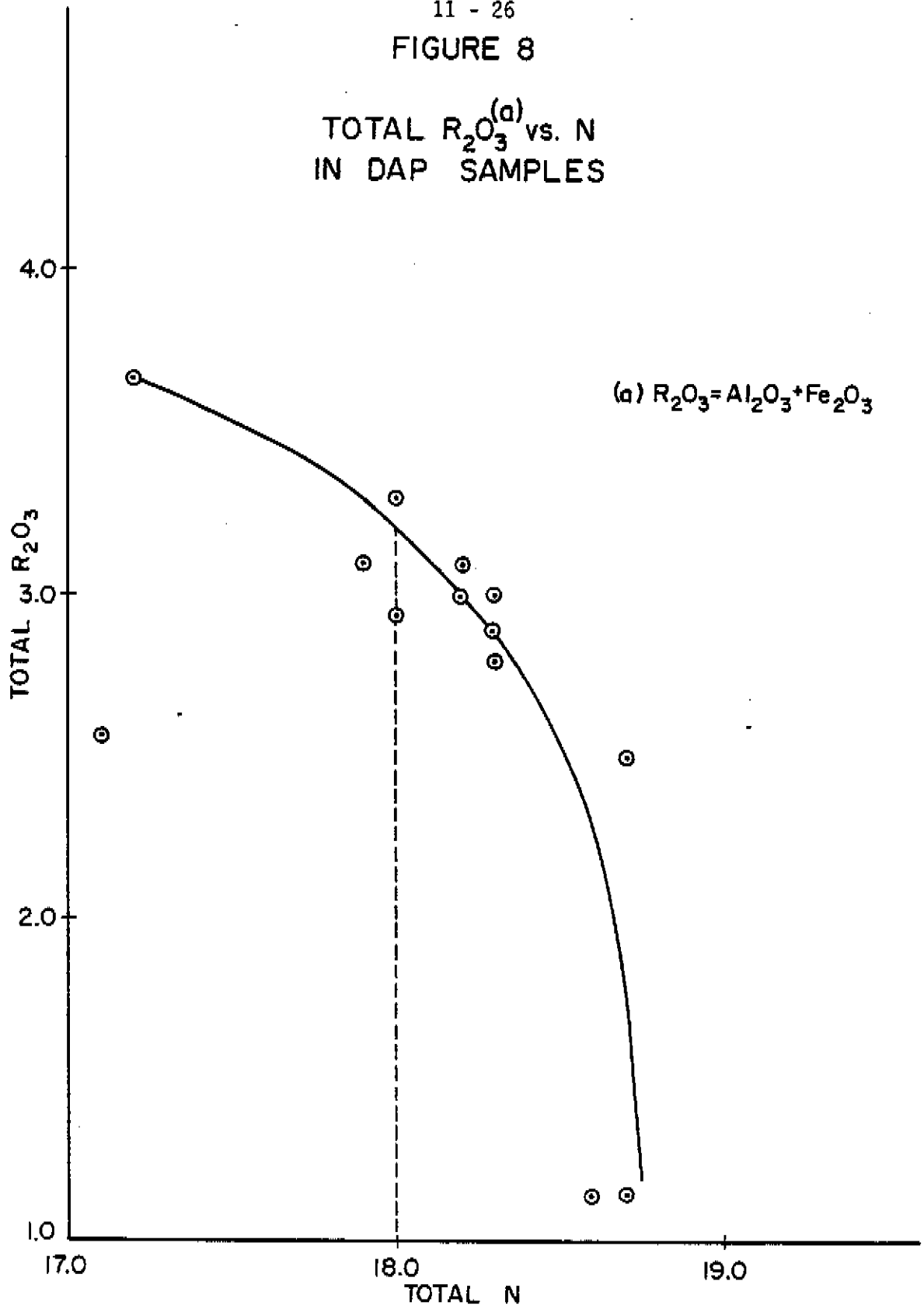


FIGURE 8

TOTAL $R_2O_3^{(a)}$ vs. N
IN DAP SAMPLES



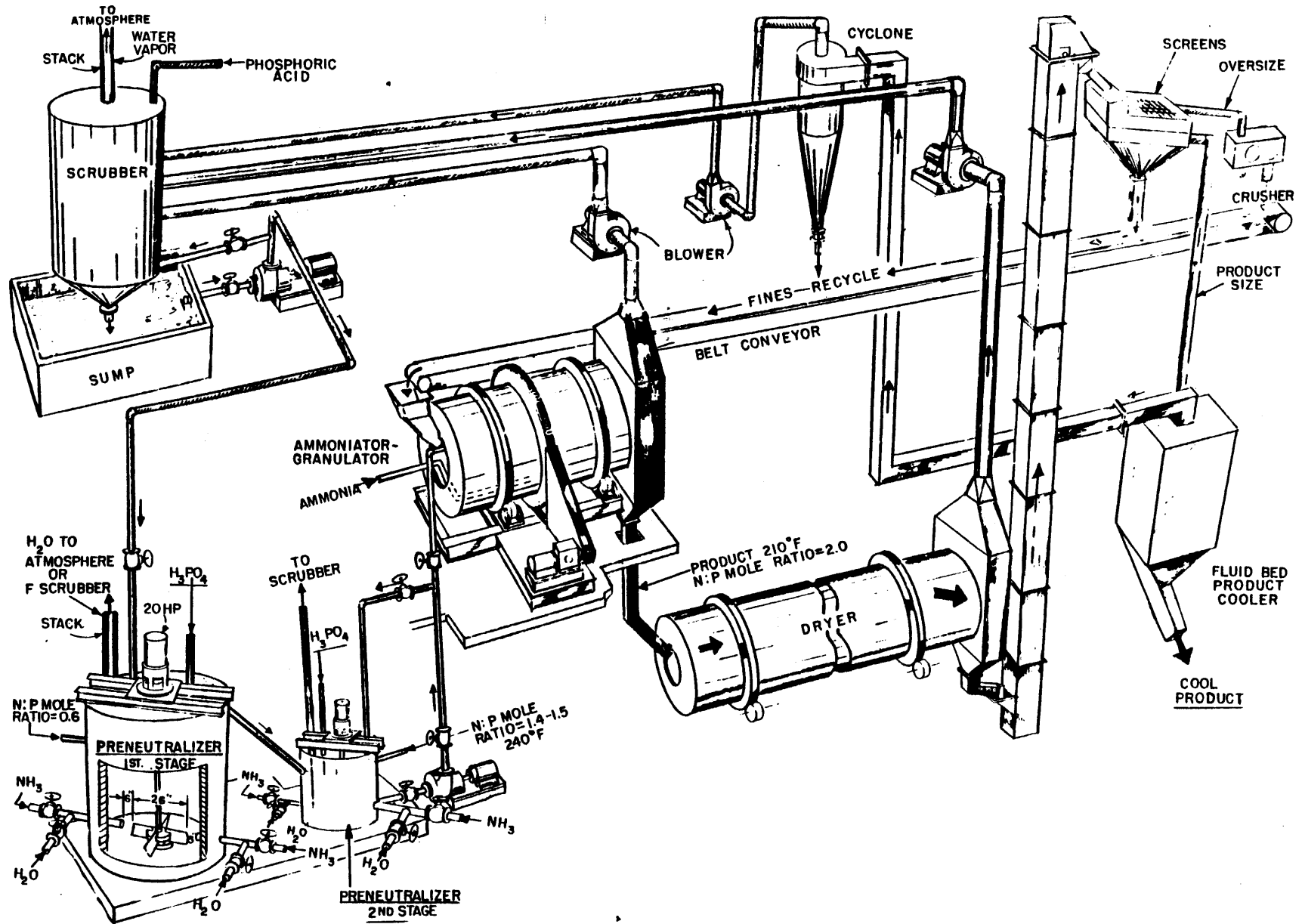


FIGURE 9

TVA PROCESS FOR PRODUCTION OF GRANULAR DIAMMONIUM PHOSPHATE

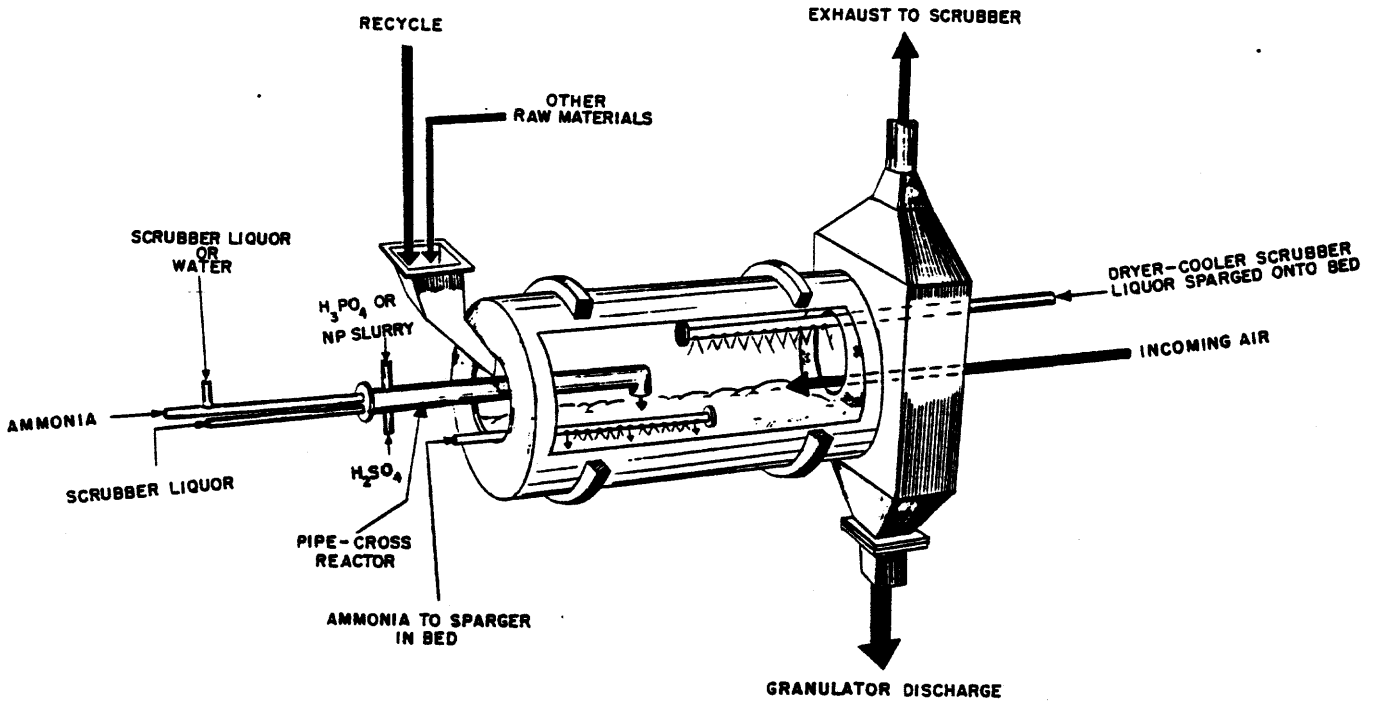


FIGURE 10
PIPE-CROSS REACTOR FOR DAP PRODUCTION

TA/80/11 Effect of impurities in wet-process phosphoric acids on DAP grades by F.P. Achorn, E.F. Dillard, A.W. Frazier, D.G. Salladay, T.V.A., USA

DISCUSSION : (Rapporteur R. Schoemaker, UKF, Netherlands)

Q - Mr. R. LOSTE, S.A. Cros, Spain

Could you indicate for making DAP:

- a) if ammonia losses from granulator are larger when using the conventional preneutraliser system or the pipe reactor system
- b) if this difference may be quantified?

A - During the production of DAP, the losses from the preneutraliser and the TVA pipe cross reactor are essentially the same because they are both operated at the same N:P mole ratio and slurry temperature. Usually, the N:P mole ratio is 1.45 and the slurry temperature about 120° C. With these conditions, the ammonia loss is about 5% of total NH₃ input.

Q - Mr. A. VILLARD, APC Rouen, France

What is your opinion as to the role of aluminium in the increased viscosity and in the possible interaction between aluminium and fluorine?

A - Aluminium has a slight effect on increased viscosity of the slurry in the preneutraliser; however, the leading contributors to high viscosity are Fe and Mg. In slurries, low in F-content, an amorphous Fe-NH₄-PO₄-nH₂O gel forms. In a system low in Al and Fe, but high in Mg, usually the Mg combines with F and P to form a Mg-NH₄-PO₄-nH₂O amorphous gel. The latter compound forms, when there is insufficient Al and Fe to react with the F of the slurry.

Q - Mr. C. HOEK, DSM, Netherlands

What really is the relation between the data of table 1 and the graphs of the figures 1 to 8? E.g., fig. 1 two points on the 18% N-line with 7.2 and 7.6% impurities, but in the data you see 8.4 and 7.6: I am missing the points M and N.

A more important question is related to statistics. In most of your figures, the point L is playing an important role. Have you done calculations about the statistical significance of the conclusions?

A - No, we did no statistical calculations, but there were more points available than shown in the graphs.

Q - Mr. O. NEVES, Luchsinger, Brazil

Can you give an idea of maximum temperature achieved in pipe reactor for prevention of insoluble P₂O₅ in product?

A - In the production of DAP, the formation of insoluble P₂O₅ in the TVA pipe cross reactor is not temperature related.

Q - Mr. J.H. FOURIE, Foskor, South Africa

What is the effect of low Fe_2O_3 , low Ca, but MgO-content between 0.8% and 1.5% on viscosity of slurry in DAP production? F: Fe_2O_3 ratio still ± 5.7 ?

A - Results in high viscosity of slurry from preneutraliser. Small scale tests show that magnesium can cause high viscosity problems in the preneutraliser if an excess of fluorine is present over the amount needed to precipitate the iron and aluminium as $(\text{Al,Fe})\text{-NH}_4\text{-PO}_4\text{-F-H}_2\text{O}$. The precipitate in this case is an amorphous $\text{MgNH}_4\text{HFPO}_4$ compound. The obvious way to avoid this compound is to defluorinate the acid. This can be accomplished by operating the ammoniator scrubbers at a low N:P mole ratio (less than 0.3) so that the F can be removed in the scrubbers.

Q - Mr. M. R. MONALDI, Montedison SpA, Italy

Tables 5, 6, 7 show an increase of free water with decreasing grades of DAP. Is that due to a casual behaviour or is there any difficulty during the drying step deriving from impurities present in DAP at lower grade?

A - The difficulty in drying does increase as the Fe and Al increase because these are granulation promoters. Their increase will tend to cause the particle size of the recycle load to increase which tends to increase the drying requirements. However, these are really insignificant changes and the increased amounts of Fe and Al improve the storage characteristics of the DAP.

Q - Mr. B. MANSOUR, SIAPE, Tunisia

What is the influence of acid impurities on the physical quality of DAP granules (hardness)?

A - Impurities such as Fe and Al improve the storage characteristics of DAP. Less is known about the effect of Mg. Some researchers believe that, when the acid has a low Al and Fe content and relative high F and Mg contents, an amorphous $\text{Mg-NH}_4\text{-PO}_4\text{-F-nH}_2\text{O}$ compound forms which may cause caking of the DAP in storage. Generally, Fe and Al cause the product to become harder than those produced from pure phosphoric acid. Also DAP, 18-46-0 grade, that contains relatively large amounts of Fe and Al (P_2O_5 2.0%) has a higher critical humidity than does pure DAP, 21-53-0 grade.

Q - Mr. T.R. BOULOS, National Research Centre, Cairo, Egypt

What do you think will be the solution with F-deficient ores to counteract the higher viscosity of acid slurry?

A - Prior to ammoniation of the acid, ensure that there is sufficient ageing and clarification of the acid to remove Al, Fe, Ca and Mg.

Q - Mr. J.Th. BOONTJE, UKF, Netherlands

a) On page 11-6 of your lecture, you suggest to make NH_4F by mixing F-bearing gases with NH_3 -bearing gases. Are you not afraid of mist formation?

b) Did you determine the crystal phase of the $(\text{NH}_4)_2\text{SiF}_6$ in your samples being - or -modifications? (table 4,5,6,7)

- A -
- a) The best way to obtain NH_4F is to form it in the reactor (preneutraliser) by reacting HF from the tail gas scrubber with ammonia added to the preneutraliser. In the US, tail gas scrubbers are frequently used to scrub exit gases from the granulator scrubber. HF is in the exit gas stream from the granulator scrubber because it is usually operated at a N:P mole ratio of 0.3. Ammonium fluoride can also be produced by reacting ammonia with $\text{H}_2\text{SiF}_6 \cdot n\text{H}_2\text{O}$. The NH_4F is separated from the SiO_2 , $n\text{H}_2\text{O}$ by decantation.
- b) We did not try to determine if the $(\text{NH}_4)_2\text{SiF}_6$ in the samples was in the - or -form. The values for $(\text{NH}_4)_2\text{SiF}_6$ were calculated by using microscopic and chemical analysis.

Q - Mr. M. GAURON, Cofaz, France

My question relates to the composition of the DAPs described in table 4 and 5. They both contain aluminium fluorophosphate, one contains iron fluorophosphate and the other not. Can you describe the physical method which allows to distinguish between these two constituents in the fertiliser matrix? Is the microscopic test sufficient?

- A -
- Most of these compounds were determined by using a combination of microscopic and chemical analysis. The results were confirmed by other analyses such as Argon Plasma Emission spectrometry, X-ray diffraction and Fourier Transform Infrared spectroscopy.