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SOME AGRONOMIC IMPLICATIONS ON USE OF LOW-GRADE PHOSPHATE ROCK

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Many industry representatives have reported there are, or soon will be, shortages of high-grade phosphate rock in Central Florida. Some report that the supply of high-grade rock will be exhausted by the end of this decade (1). Most Florida companies reserve high-quality (high-analysis) rock for shipment and use low-grade rock containing 62 to 68 BPL in their own phosphoric acid plants. About 40 percent of U. S. phosphate rock is exported as rock or as upgraded products (2). Exports of phosphate rock are increasing; this will cause even more low-grade rock to be used by U. S. producers of finished phosphate products such as diammonium phosphate of 18-46-0 grade (DAP), monoammonium phosphate (MAP), and triple superphosphate (TSP). Use of lower-grade rock has increased the amount of impurities in phosphoric acid because of increased impurities introduced by the rock and because of different operating conditions required to effectively use the rock. As a consequence, many producers find it difficult to meet grade tolerances for DAP and TSP. Some producers have lowered their TSP grade from 46 to 44 percent available P_2O_5. Others are having difficulty meeting the P_2O_5 requirements of commercial DAP.

Diammonium Phosphate

During this past year TVA analyzed both chemically and microscopically, more than 30 samples of commercial DAP. Chemical analyses of products from 9 different typical producers are shown in table 1. Three samples (33%) did not meet total P_2O_5 requirements and two (22%) did not meet the nitrogen requirement. Of 30 samples analyzed, 39 percent did not meet some grade requirements, 11 percent did not meet both N and P_2O_5 requirements, 22 percent failed to meet nitrogen requirements, and 6 percent did not meet P_2O_5 requirements. Chemical analyses show water-soluble P_2O_5 to be about 85 to 90 percent of the available P_2O_5 instead of the 95 percent formerly obtained when high-grade rock was used.

One reason for low N and P_2O_5 contents in DAP is excessive $CaSO_4$ in the phosphoric acid used to produce the DAP. High iron content coupled with high retention times in the preneutralizer can cause relatively high contents of citrate-insoluble P_2O_5 in the DAP product. Both of these problems can be eliminated. Calcium sulfate level can be decreased by operating the reactors at lower temperatures and by improved maintenance of the filter cloth. Iron can be eliminated by decreasing retention time in the preneutralizer. It is suggested that this can be easily accomplished by replacing the preneutralizer with TVA's pipe-cross reactor (PCR). Citrate-insoluble P_2O_5-Fe_2O_3 compounds do not form when this reactor is used because slurry retention time in the PCR is very low.

Table 1 shows that sulfur contents of these DAP products average about 2 percent, with some products containing as much as 3.8 percent. Some agronomists have made agronomic response tests using DAP containing 3.0 percent sulfur. In those tests it was assumed that the sulfur content of DAP was nil or nonexistent. As a result, the check strip would not show sulfur deficiency. In designing field trials some credit for sulfur in DAP should be considered. The sulfur content of MAP is usually about the same as that of DAP. Sulfur content of ammonium polyphosphate solutions is much less than that of DAP because most of the gypsum has been removed from the superphosphoric acid used to produce these solutions. Therefore, sulfur content of a commercial 10-34-0 is about 0.5 percent.

Of other impurities present in DAP, probably the most significant is iron. The Fe_2O_3 contents of the products shown in table 1 average about 1.5 percent (1.05% Fe). In many uranium recovery processes extra iron is added to the phosphoric acid and ends up in the DAP product. Other impurities are not present in large enough quantities to be considered agronomically.

Table 2 shows a breakdown of all compounds found in an off-grade DAP. The product has a low analysis because of the relatively large quantity (about 6%) of large crystals of citrate-insoluble $FeNH_4(HPO_4)_2.5H_2O$ in the product. Table 3 shows compounds present in DAP which meet grade requirements. Note the small quantity (0.8%) of citrate-insoluble $FeNH_4(HPO_4)_2.H_2O$.

Triple Superphosphate

Chemical analyses of several samples of commercial TSP are shown in table 4. Note that in the 1950's and 1960's contents of available P_2O_5 in triple superphosphate usually averaged well above 47 percent. This past year many companies have decreased the content of guaranteed available P_2O_5 to 44 percent. This has been caused by more impurities in rock and acid used to produce TSP. Dominant impurities are calcium, iron, sulfur, and aluminum. Increasing amounts of impurities affect physical characteristics of the product so that it becomes very difficult to screen the product during its production. To avoid these problems, usually the acidulation ratio (P_2O_5 from acid--P_2O_5 from rock) is decreased which results in a product that can be screened; however, the resulting P_2O_5 availability is decreased. This problem has become more apparent in TSP production than for other phosphate products because TSP is usually used as a convenient means of disposing of impurities that settle in the clarification of wet-process phosphoric acid. The acid is usually clarified by allowing sludge which forms during aging of the acid to settle as solids. These solids are then added to the acid used to produce TSP; the purer acid is either shipped as acid or converted into ammonium phosphates (DAP or MAP).

Data in table 4 show that water-soluble P_2O_5 in TSP has been steadily decreasing. Recent samples contained as little as 78 percent of available P_2O_5 as water-soluble P_2O_5. This is about 20 percent less than the 95 percent formerly obtained when TSP was produced from high-grade rock.

Because of more stringent restrictions imposed by the Environmental Protection Agency, many phosphate producers have installed scrubbers for removing SO_3 from their sulfuric acid plant stacks. Ammonia is added to neutralize the scrubber liquor thereby producing a solution of ammonium sulfate. Rather than add more energy and processing costs to this solution to produce solid ammonium sulfate, some producers add the ammonium sulfate solution into digestion tanks of the TSP plant. Naturally, this causes sulfur content of the product to increase. Some recent samples of TSP were analyzed for sulfur; these results are also shown in table 4 (samples I and J). These data show sulfur contents to be as high as 1.4 percent. Unfortunately, the TSP was not analyzed for iron; however, other data indicate that TSP contains 1 to 2 percent iron.

Summary

These data show that most commercial ammonium phosphates and triple superphosphates contain significant amounts of sulfur and iron. Although sulfur content is not sufficient to correct most sulfur-deficient soils, it should be considered as a source of sulfur. This sulfur usually is present as agronomically available sulfate-sulfur. Iron is present in the ferrous form. The iron content in many instances may be large enough to supply needs of some crops. We can assume that P_2O_5 availability will continue to be 46 percent DAP and probably 44 percent for TSP. Therefore, there would be little or no effect of unavailable P_2O_5 added through these products.

Data show a dramatic decrease in the water-soluble P_2O_5 in TSP; however, TVA agronomists indicate that these water-soluble P_2O_5 contents are sufficient for practically all crops grown in most soils. Most TSP products are minor but significant sources of sulfur and iron.

Analyses of both ammonium phosphates and TSP show that they do not contain significant quantities of other micro- or secondary nutrients.

References

1. Williams, James M. "Beneficiation of Low-Grade Florida Phosphate Ore and Resulting Product Quality," Second Chemical Congress of the North American Continent, August 25-28, 1980

2. TVA's Fertilizer Trends 1979 (Bulletin Y-150), National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama

3. Achorn, F. P., E. F. Dillard, A. W. Frazier, and D. G. Salladay. "Effect of Impurities in Wet-Process Phosphoric Acids on DAP Grades," presented at the ISMA Conference, Vienna, Austria, November 11-13, 1980

Table 1

Chemical Analyses of Typical Commercial DAP Samples

		P_2O_5											
Company	Total N	Total	Water Sol.	Water Sol. as % of Avail.	C.I.	Avail.	CaO	Fe_2O_3	Al_2O_3	MgO	S	F	H_2O
A	18.3	46.5	42.06	90.6	0.07	46.4	0.44	1.60	1.30	0.69	1.3	2.4	1.8
B	18.3	46.5	41.30	89.6	0.37	46.1	0.29	1.80	1.20	0.62	2.0	1.2	1.7
C	18.7	47.4	44.40	93.7	Nil	47.4	1.30	0.67	0.48	0.70	1.7	1.4	1.9
D	18.3	47.3	42.48	91.4	0.84	46.5	0.40	1.70	1.10	0.58	1.4	1.7	2.3
E	17.1	44.8	38.75	87.5	0.46	44.3	1.80	0.86	1.70	0.63	1.7	3.2	-
F	17.9	45.2	40.86	90.4	0.01	45.2	0.76	1.50	1.60	0.55	1.6	2.7	-
G	18.7	45.3	40.76	90.2	0.08	45.2	0.43	1.10	1.40	0.55	1.7	2.5	-
H	18.4	48.2	42.24	88.6	0.49	47.7	0.08	1.12	1.97	0.08	3.8	1.7	0.6
I	18.9	47.5	42.74	90.0	0.05	47.5	0.18	1.80	1.62	0.67	1.0	2.3	0.7
J	18.2	46.2	-	-	0.05	46.2	0.46	1.70	1.30	0.71	1.4	2.4	2.1
K	18.0	46.2	-	-	0.31	45.7	0.42	1.90	1.20	0.72	1.7	1.8	2.2

Table 2

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

Solid	Wt %	F	Ca	N	P_2O_5	Fe	Al	Mg	SO_4	Zn	V	Cr	Cd	U	Ni	Mn
$MgNH_4PO_4.6H_2O$	2.66			0.22	1.14			0.39								
$Ca_4SO_4AlSiF_{13}.12H_2O$	0.72	0.23	0.15				0.02		0.09							
$ZnNH_4PO_4$	0.01			0.001	0.004					0.004						
$CdNH_4PO_4$	0.001			0.0001	0.0003								0.0005			
$UO_2NH_4PO_4$	0.03			0.001	0.006									0.020		
$NiNH_4PO_4$	0.004			0.0003	0.002										0.001	
$MnNH_4PO_4$	0.09			0.008	0.038											0.029
$FeNH_4(HPO_4)_2$	5.95			0.30	3.07	1.21										
$Al\text{-}NH_4\text{-}PO_4\text{-}F\text{-}H_2O$	4.71	1.00		0.37	1.87		0.71									
$V\text{-}NH_4\text{-}PO_4\text{-}F\text{-}H_2O$	0.06	0.01		0.004	0.021						0.015					
$Cr\text{-}NH_4\text{-}PO_4\text{-}F\text{-}H_2O$	0.02	0.004		0.001	0.007							0.005				
$Ca(NH_4)_2(HPO_4)_2.H_2O$	4.22		0.59	0.41	2.10											
$(NH_4)_2SiF_6$	0.78	0.50		0.12												
$(NH_4)_2SO_4$	6.59			1.40					4.79							
$(NH_4)_2HPO_4$	66.08			14.02	35.54											
$(NH_3)_3PO_4$	4.20			1.15	1.88											
Free H_2O	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

Table 3

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

Solid	Wt %	F	Ca	N	P_2O_5	Fe	Al	Mg	SO_4	Zn	V	Mn	Cr	Cd	U	Ni	Si
$MgNH_4PO_4.H_2O$	2.92			0.25	1.25			0.43									0.01
$Ca_4SO_4AlSiF_{13}.12H_2O$	0.36	0.11	0.07				0.01		0.04								
$ZnNH_4PO_4$	0.02			0.002	0.008					0.0073							
$CdNH_4PO_4$	0.0004			0.00002	0.0002									0.0002			
$UO_2NH_4PO_4$	0.03			0.001	0.006										0.02		
$NiNH_4PO_4$	0.005			0.0004	0.002											0.002	
$MnNH_4PO_4$	0.11			0.009	0.047							0.036					
$FeNH_4(HPO_4)_2$	0.84			0.04	0.43	0.17											
$Fe\text{-}NH_4\text{-}PO_4\text{-}F\text{-}H_2O$	3.78	0.69		0.25	1.29	1.02											
$Al\text{-}NH_4\text{-}PO_4\text{-}F\text{-}H_2O$	4.44	0.94		0.35	1.76		0.67										
$V\text{-}NH_4\text{-}PO_4\text{-}F\text{-}H_2O$	0.06	0.01		0.004	0.021						0.015						
$Cr\text{-}NH_4\text{-}PO_4\text{-}F\text{-}H_2O$	0.03	0.006		0.002	0.01								0.0076				
$Ca(NH_4)_2(HPO_4)_2.H_2O$	1.86		0.26	0.18	0.92												
$(NH_4)_2SiF_6$	1.08	0.69		0.17													0.17
$(NH_4)_2SO_4$	5.71			1.21					4.15								
$(NH_4)_2HPO_4$	73.1			15.5	39.32												
$NH_4H_2PO_4$	1.85			0.23	1.14												
Free H_2O	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 4

Chemical Analyses of Commercial Triple Superphosphate (TSP)

Year	Sample Designation	Avail. P_2O_5	Water Sol. P_2O_5	Total P_2O_5	% Avail. of Total P_2O_5	Water Sol. P_2O_5 as % of Avail.	Mg	S	N
1954	A	47.39	43.25	48.24	98.2	91.3	0.19	-	-
1955	B	47.71	38.75	48.55	98.3	81.2	0.28	-	-
1956	C	48.30	41.42	48.79	99.0	85.8	0.28	-	-
1960	D	47.78	41.75	48.59	98.3	87.4	0.35	-	-
1979	E	46.70	39.10	47.60	98.1	83.7	0.36	-	-
1979	F	45.00	40.00	46.34	97.1	88.9	0.73	-	-
1979	G	47.19	36.91	47.52	99.3	78.2	0.45	-	-
1979	H	44.75	37.70	46.92	95.4	84.2	0.36	-	-
1980	I	45.00	38.80	47.3	95.1	86.2	-	1.40	0.17
1980	J	43.70	37.80	45.7	95.6	86.5	-	1.07	0.05