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EFFECTS OF IMPURITIES ON PRODUCTION OF DIAMMONIUM PHOSPHATE

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INTRODUCTION

The abundance of high quality commercial phosphates is declining worldwide. It is expected that the high-grade phosphate rock resources from present commercial phosphate mines will gradually be depleted and replaced by lower grade rock containing more impurities. Also, the opening of new phosphate deposits may produce phosphate rock containing significantly different levels of impurities than those of present commercial rocks.

In late 1982, an exploratory pilot plant scale Diammonium Phosphate (DAP) production study was run using wet-process phosphoric acid containing various levels of added impurities. The equipment used for the study was International Fertilizer Development Center's (IFDC) Pilot Plant at Muscle Shoals, Alabama, U.S.A.

The main objective of the study was to make a preliminary evaluation of the effects of three major impurities -- iron, aluminum, and magnesium -- on the production of DAP and on the product's chemical and physical properties.

DESIGN OF THE EXPERIMENT

The granulation pilot plant tests were conducted according to a two-level, three-variable factorial design.

A baseline 40% P_2O_5 acid was prepared in IMC's New Wales plant from a selected central Florida phosphate rock. The acid was cooled, aged, then shipped to IFDC in three tank cars. The baseline acid had the following composition (wt.%):

Table 1

P_2O_5	39.70	CaO	0.05	SO_3	3.18
Al_2O_3	1.15	MgO	0.86	Fe_2O_3	1.09
F	1.82	SiO_2	0.71	H_2O	37.16

Immediately before each test run, the baseline acid was "spiked" with different levels and combinations of Al^{3+} , Mg^{2+} , and Fe^{3+} . To perform this "spiking," alumina, magnesium

fluosilicate, and iron powder were used. Bench scale work had established that a clarified acid "spiked" with these impurities would produce essentially the same solids upon aging as a commercial acid with the same level of impurities. It was recognized that large amounts of fluorine are associated with the magnesium in magnesium fluosilicate and therefore the results of the experiments confounded the effects of magnesium with those of fluorine. This magnesium-fluorine confounding was accepted, and it was decided to run with the confounding at first and then make additional tests to separate the effects of magnesium and fluorine. On test efforts requiring high iron, hydrogen peroxide was also added to oxidize part of the dissolved Fe^{2+} to Fe^{3+} . The amount added was that required to return the electromotive force (EMF) of the acid to the value found in the unspiked baseline phosphoric acid.

The factorial test required eight test efforts, together with three midpoint replicates, to establish the linearity and variance of the results. Besides these eleven test efforts, the following isolated tests were also included: (1) A test with high Mg^{2+} but lower F^- by using magnesium sulfate rather than magnesium fluosilicate, (2) A test with high Fe^{2+} , (3) A test with high Mg^{2+} and high Fe^{3+} but lower F^- .

The high and low values of the different impurities were computed as weight ratios relative to P_2O_5 . Low values were accepted as those present in the baseline acid. High and intermediate (midpoint) values were obtained after addition of impurities to the baseline acid. Following are the actual ratios obtained upon averaging results from three laboratories:

Table 2

	<u>Obtained</u> <u>$\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$</u> <u>Weight Ratio</u>	<u>Obtained</u> <u>$\text{MgO}/\text{P}_2\text{O}_5$</u> <u>Weight Ratio</u>	<u>Obtained</u> <u>$\text{Fe}_2\text{O}_3/\text{P}_2\text{O}_5$</u> <u>Weight Ratio</u>	<u>Obtained</u> <u>$\text{F}/\text{P}_2\text{O}_5$</u> <u>Weight Ratio</u>
High	0.0360	0.0420	0.0505	0.0714
Midpoint	0.0312	0.0298	0.0392	0.0492
Low	0.0281	0.0191	0.0253	0.0370

This is equivalent to the following values in 68 BPL Rock (31.1% P_2O_5)

	Al_2O_3	MgO	Fe_2O_3
High	1.12	1.31	1.57
Midpoint	0.97	0.93	1.22
Low	0.87	0.59	0.78

Table 3 contains a listing of the test efforts.

PROCESS DESCRIPTION

Three type 316L stainless steel tanks, each with a holding capacity of 4.5 m³ were used to prepare the acid treatments. During mixing, the acid was heated to about 70° - 80°C using steam coils, and cross-recirculated between the tanks. After the acid was homogeneous, batches of 1.2 m³ were transferred to a smaller heated tank which fed the pilot plant.

The IFDC pilot plant equipment and process (Figure 1) used were variations of the TVA process. The equipment arrangement closely duplicated the IMC-New Wales commercial unit. The most notable variations were: The use of a recycle heater to simulate industrial-scale recycle temperature, and the use of a positive-displacement lobe pump to move the slurry from the preneutralizer to the granulator.

Phosphoric acid, with the prescribed content of impurities, was fed at a controlled rate to a recirculation tank of a Venturi-type scrubber used to clean the exhaust gas from the drum granulator. It was desired that the resulting liquor from this scrubbing would contain enough nitrogen to maintain a NH₃/H₃PO₄ mole ratio between 0.40 and 0.50; therefore, extra ammonia was added directly to the granulator off-gases to maintain the desired mole ratio. The liquor holding capacity of the scrubbing system was 300 liters. Foaming in the scrubbing system and in the preneutralizer was controlled by using a sodium salt of sulfonated oleic acid. The stream from the scrubber was used to control the production rate of the plant.

The scrubber liquor was introduced into the preneutralizer above the liquid level. The preneutralizer was 61 cm in diameter and 207 cm deep. The agitator was fitted with axial-flow, downward-thrust turbines. The normal depth of slurry in the preneutralizer was about 62 cm above the cone which is equivalent to retention times of about 55-98 minutes depending on production rates. Ammonia is injected in at a level with the bottom turbine blade. The temperature of the slurry was maintained between 110°C and 116°C.

Slurry was transferred to the granulator by a variable speed positive displacement pump. A drilled pipe slurry distributor fitted with an air atomizer was used to distribute the slurry onto the bed.

The drum granulator was 92 cm in diameter and 1.8 m long. A 15 cm retaining dam was located 61 cm from the discharge end. The granulator was operated at a rotational speed of 16 RPM, which is equivalent to 36% of its critical speed. Ammonia gas was fed to the granulator through a drilled pipe sparger.

The rotary dryer was 92 cm in diameter and 7.3 m long. It was operated cocurrently. Its operational speed was 7 RPM. The superficial velocity of the gases through the dryer was about 2.7 m/second.

Screening was done using a 3.35 mm opening oversize screen, and a 1.18 mm undersize screen. Oversize material was routed to a single shaft chain mill. Undersize material together with a fraction of the product, was returned to the granulator as recycle.

The recycle heater was operated to maintain recycle temperature at about 75°C at the inlet to the drum granulator which is closer to commercial plant conditions than the 40°C which otherwise would have been obtained due to the large heat losses typical of small capacity pilot plants.

DAP PRODUCTION

The DAP production test efforts were run in random order. Each effort consisted of three main tasks: (1) Addition of the impurities to the baseline acid. (2) Several short test runs (at least 5 hours) to flush out and condition the startup recycle material. (3) An extended test run of about 11 hours. Average conditions and samples were taken during the latter part of each of these test runs.

Target variables were:

Production Rate: 250 kg/hour
 Recycle/Product Ratio: 4
 NH₃/H₃PO₄ mole ratio of preneutralizer slurry: 1.45
 Recycle Temperature: 75°C
 Preneutralizer Slurry Temperature: 110°C-116°C
 Ammonia addition to drum granulator: 170% of
 stoichiometric

A summary of data taken on the extended runs is listed in Table 4.

RESULTS

Tables 5, 6, 7, and 8 contain results from the analytical and physical measurements carried out on the products.

In general, the results of these studies show, as expected, that the original products are rather similar in their basic composition. The main components in the products are DAP, Ammonium Sulfate, and Monoammonium Phosphate with small amounts of other minor constituents.

Chemical analyses of the water insoluble (W.I.) fractions and solid phase identification carried out at both IFDC and the Tennessee Valley Authority (TVA) do reveal several facts that should be of interest to the Fertilizer Industry. TVA was able to newly characterize the salt $MgAl(NH_4)_2H(PO_4)_2F_2$. This salt was correlated with high citrate insoluble (C.I.) P_2O_5 and the salt's formation related to long retention time in the reactor during production. This material has been seen in commercial products, and its degree of citrate solubility decreases with increasing crystal size.

The choice in operation, therefore, seems to be between the citrate soluble amorphous gels with their operating problems and the formation of citrate-insoluble crystalline products that do not significantly affect operations.

A statistical correlation of the variables versus C.I. P_2O_5 and W.I. fraction are shown in Table 9.

The main surprise from this correlation is that there is no significant effect of Aluminum in the starting acid on the Aluminum in the W.I. fraction. However, the fact that relatively high levels of fluorine were present in all the experiments may explain this absence of effect. The power of fluorine to complex aluminum is well known.

A linear regression procedure was carried out on the data. No significant twofold or threefold interactions were detected. All the resulting models were linear, with the exception of the preneutralizer slurry viscosity which showed a logarithmic response to the Al_2O_3/P_2O_5 weight ratios. The model pertaining to the end product grade is

$$(1) \quad N (\%) \quad = \quad 20.83 - 47.41 X_1 - 18.02 X_2 - 15.59 X_3$$

$$(2) \quad \text{Total } P_2O_5 \quad = \quad 47.98 + 70.17 X_1 - 69.54 X_2 - 23.34 X_3$$

Where: $N(\%)$ = Total N in end product on dry basis

Total $P_2O_5(\%)$ = Total P_2O_5 in end product on a dry basis

X_1 = Al_2O_3/P_2O_5 weight ratio in feed acid

X_2 = MgO/P_2O_5 weight ratio in feed acid

X_3 = Fe_2O_3/P_2O_5 weight ratio in feed acid

Basically, the results show no exotic chemical reaction. The factors associated with the $\text{Fe}_2\text{O}_3/\text{P}_2\text{O}_5$ and $\text{MgO}/\text{P}_2\text{O}_5$ term fit a dilution model well. However, the factors associated with the Al_2O_3 are greater than explained by dilution. But when the extended runs are modeled with differences in MAP produced along with the DAP, it becomes apparent that the high aluminum runs shifted the production toward greater MAP, less DAP; thus the positive term for the P_2O_5 factor, and corresponding negative term for % N. This effect is considered to be due to mass transport effects caused by high viscosities during the run along with the dilution effect.

SUMMARY

A summary of the effects of the impurities studied on the grade and physical properties of DAP produced and on the granulation pilot plant operation are listed as follows:

1. Aluminum showed the most severe effects on operations. It affected the DAP grade by decreasing the ability to incorporate nitrogen (probably through effects on mass transfer) thus decreasing the $\text{NH}_3/\text{H}_3\text{PO}_4$ mole ratio. Also, it was the greatest contributor to increased viscosity of preneutralizer slurry with the result that the pilot plant production rate had to be decreased to be able to pump and distribute the slurry in the granulator. On the other hand, products made with acids having a high aluminum content exhibited decreased moisture penetration during bulk storage at high moisture conditions.
2. Iron addition showed the most effect on nitrogen grade, but showed less effect than aluminum on a weight-for-weight basis on plant operation. Iron did adversely affect preneutralizer viscosities but not to the same degree as aluminum. No iron effect was noted upon the physical properties of the end products.
3. Magnesium also lowered nitrogen grade but not to the degree that iron does. The magnesium also had a tendency to lower C.I. P_2O_5 . However, it is felt this is due to the fluorine added with the magnesium. Granulation improved with magnesium as did the preneutralizer slurry fluidity. Products made from acids with high magnesium were more hygroscopic, which adversely affects their storage properties. A test using magnesium sulfate in supplying magnesium to the feed acid did not show significant differences from the high magnesium-high fluorine test, except for the C.I. percentage.

Basically the results show that there is little chemical interaction among the impurities but rather their effects are the normal combining weight reactions and the grade dilution one would expect from these chemicals. Therefore, as phosphate rocks tend to run toward any particular impurity such as MgO, it can be offset by lowered quantities of the other impurities without compromising the final grade of DAP.

The work also reinforces work that has shown citrate insoluble P_2O_5 is not an effect of the iron, aluminum, or magnesium (within the boundaries of the test work) but rather is affected by the operating conditions in the reactor along with the level of fluorine present. Higher fluorine levels tended to reduce C.I. P_2O_5 as well as reduce reactor viscosities.

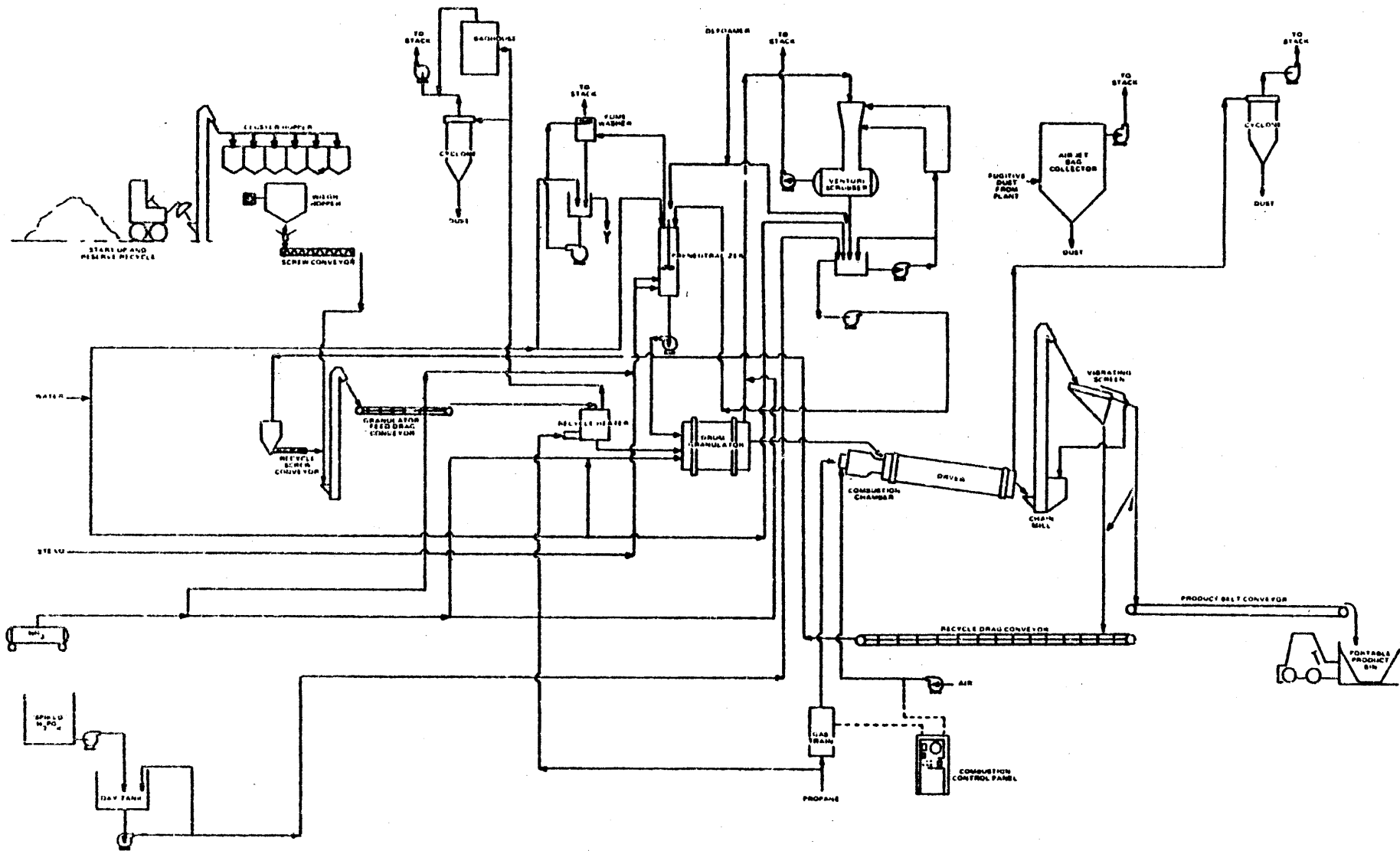


Figure 1 IFDC's Pilot Plant for the Production of DAP.

Table 3. Description of Extended Test Runs

<u>Acid Treatment</u>	<u>Test</u>	<u>Date</u>	<u>Part of the Statistical Design</u>	<u>Value of Impurity/P₂O₅ Weight Ratio in the Acid</u>			
				<u>Al₂O₃ P₂O₅</u>	<u>MgO P₂O₅</u>	<u>Fe₂O₃ P₂O₅</u>	<u>F P₂O₅</u>
Baseline	7-187	7/29/82	Yes	Low	Low	Low	Low
A	7-206	10/1/82	Yes	High	Low	Low	Low
B	7-191	8/12/82	Yes	Low	High	Low	High
AB	7-212	10/20/82	Yes	High	High	Low	High
C	7-197	8/31/82	Yes	Low	Low	High	Low
AC	7-204	9/23/82	Yes	High	Low	High	Low
BC	7-200	9/13/82	Yes	Low	High	High	High
ABC	7-208	10/7/82	Yes	High	High	High	High
Midpoints I	7-202	9/17/82	Yes	Midpoint	Midpoint	Midpoint	Midpoint
Midpoints II	7-210	10/14/82	Yes	Midpoint	Midpoint	Midpoint	Midpoint
Midpoints III	7-216	10/29/82	Yes	Midpoint	Midpoint	Midpoint	Midpoint
B (low F)	7-214	10/25/82	No	Low	High	Low	Low
BC (low F) ^a	7-199	9/8/82	No	Low	High	High	High ^a
C (no H ₂ O ₂)	7-218	11/4/82	No	Low	Low	High	Low

a. Although it was intended to have a low F/P₂O₅ weight ratio in this test run by defluorinating the acid through heating, chemical analyses showed high F/P₂O₅ weight ratios in the feed phosphoric acid and in the screened product.

Table 4 Summary of Average Data Collected During Extended Pilot-Plant Test Runs Producing DAP

Acid Treatment	Baseline	A	B	AB	C	AC	BC	ABC
Test	7-187	7-206	7-191	7-212	7-197	7-204	7-200	7-208
Date	7-29-82	10-1-82	8-12-82	10-20-82	8-31-82	9-23-82	9-13-82	10-7-82
Calculated production rate, kg/hour ^b	255	213	260	290	178	188	249	189
Test duration, hour ^c	7.7	11.6	12.3	11.4	8.7	11.4	11.2	7.6
Period averaged, hour:minute	12:00-15:30	17:30-19:30	18:00-20:00	17:30-19:30	17:30-19:30	18:00-19:30	18:00-20:00	14:00-16:00
Granulator scrubber:								
Acid feed rate, kg/hour ^b	302	236	301	314	206	226	285	206
Ammonia feed rate, kg/hour	0.0	8.6	12.5	8.5	8.0	0.0	9.1	14.5
NH ₃ /H ₃ PO ₄ mole ratio/liquor ^d	0.423	0.476	0.386	0.430	0.416	0.495	0.430	0.535
Temperature of liquor, °C	42	50	47	50	50	37	50	55
Residence time, minute	92	134	99	97	146	131	101	134
Preneutralizer:								
Liquor feed rate, kg/hour	293	216	285	297	196	212	277	196
Ammonia feed rate, kg/hour	51.7	66.5	47.6	62.5	62.6	47.4	42.1	65.7
NH ₃ /H ₃ PO ₄ mole ratio/slurry ^d	1.441	1.445	1.442	1.458	1.438	1.513	1.460	1.417
Temperature of slurry, °C	114	114	113	115	113	97	113	114
Residence time, minute	60	70	60	54	79	85	65	78
Density of slurry, kg/liter	1.525	1.518	1.522	1.530	1.503	1.544	1.548	1.489
pH of slurry ^d	6.6	6.5	6.7	6.6	6.7	6.6	6.5	6.5
Viscosity of slurry, cP ^d	68	3,844	63	118	2,040	30,000	86	975
Granulator:								
Slurry feed rate, kg/hour ^b	293	229	284	317	191	234	280	209
Ammonia feed rate, kg/hour	32.3	23.6	24.5	24.2	24.2	23.6	24.2	22.4
Ammonia feed, as a % of stoichiometric ^e	206	181	160	145	224	235	174	192
Water feed rate, kg/hour	18	26	26	26	26	26	26	27
Recycle feed rate, kg/hour	1,013	796	1,044	1,051	576	936	1,051	660
Recycle particle size median, mm ^f	2.90	2.40	2.89	3.08	2.43	2.45	3.02	2.76
Temperature of recycle, °C	75	74	74	72	68	71	75	75
Temperature of discharge, °C	75	77/818	81	82/868	71	70	79	82/868
pH of discharge ^d	7.9	7.8	8.0	7.9	8.3	8.1	7.8	7.7
Discharge particle size median, mm ^f	3.22	2.88	3.71	3.27	2.91	3.15	3.60	3.18
Recycle/product ratio ^h	4.0	3.3	4.0	3.6	3.2	5.0	4.2	3.5
Drum speed, rpm	14	16	16	16	16	16	15	16
Dryer:								
Air flow rate (outlet conditions), m ³ /hour	5,180	5,710	5,330	5,520	5,520	5,500	5,450	5,440
Air velocity (outlet conditions), m/second	2.58	2.84	2.65	2.75	2.75	2.74	2.71	2.71
Temperature of fertilizer discharge, °C	81	NA ⁱ	84	94	91	87	91	92
Temperature of air discharge, °C	93	103	94	104	103	100	100	104
Relative humidity of air discharge, % ^j	12	NA	8	4	12	5	13	NA
Relative humidity of ambient air, %	80	35	88	70	87	48	73	68
Temperature of ambient air, °C	30	27	27	21	27	23	29	21
Drum speed, rpm	7	7	7	7	7	7	7	7
Screened product:								
Maximum particle size, mm	3.35	3.35	3.35	3.35	3.35	3.35	3.35	3.35
Minimum particle size, mm	1.70	1.18	1.70	1.18	1.70	1.18	1.18	1.18
pH ^d	7.8	7.7	7.8	7.8	8.0	8.0	7.7	7.7

(Continued)

Table 4 Summary of Average Data Collected During Extended Pilot-Plant Test Runs Producing DAP (Continued)

Acid treatment	Midpoint I	Midpoint II	Midpoint III	B(low F)	BC(low F) ^a	C(no H ₂ O ₂)
Test	7-202	7-210	7-216	7-214	7-199	7-218
Date	9-17-82	10-14-82	10-29-82	10-25-82	9-8-82	11-4-83
Calculated production rate, kg/hour ^b	262	203	196	248	274	167
Test duration, hour ^c	11.8	11.2	11.5	10.8	11.3	12.0
Period averaged, hour:minute	16:00-18:00	17:30-19:00	17:30-19:00	17:30-19:30	15:30-18:30	15:30-17:30
Granulator Scrubber:						
Acid feed rate, kg/hour ^b	303	220	207	283	302	193
Ammonia feed rate, kg/hour	11.1	15.6	5.1	6.7	14.7	0.0
NH ₃ /H ₃ PO ₄ mole ratio of liquor ^d	0.450	0.503	0.463	0.446	0.404	0.490
Temperature of liquor, °C	50	49	50	45	54	37
Residence time, minute	105	146	149	103	107	141
Preneutralizer:						
Liquor feed rate, kg/hour	274	203	196	272	276	199
Ammonia feed rate, kg/hour	53.0	53.6	63.9	58.3	57.7	37.2
NH ₃ /H ₃ PO ₄ mole ratio of slurry ^d	1.454	1.455	1.455	1.440	1.468	1.458
Temperature of slurry, °C	113	114	115	114	114	115
Residence time, minute	66	75	77	62	60	85
Density of slurry, kg/liter	1.552	1.490	1.558	1.536	1.556	1.565
pH of slurry ^d	6.6	6.6	6.5	6.6	6.7	6.6
Viscosity of slurry, cP ^d	231	449	428	187	170	592
Granulator:						
Slurry feed rate, kg/hour ^b	286	211	215	273	300	180
Ammonia feed rate, kg/hour	23.6	23.6	23.6	23.3	24.4	22.7
Ammonia feed, as a % of stoichiometric ^e	154	200	207	157	161	227
Water feed rate, kg/hour	26	36	39	26	26	42
Recycle feed rate, kg/hour	979	702	657	1,030	1,039	706
Recycle particle size median, mm ^f	3.12	2.81	2.53	2.73	2.93	1.83
Temperature of recycle, °C	71	75	73	74	74	70
Temperature of discharge, °C	81	81/86 ^g	69/74 ^g	81/86 ^g	79	70/79 ^g
pH of discharge ^d	7.6	8.0	7.9	7.9	8.0	8.1
Discharge particle size median, mm ^f	3.52	3.31	3.00	3.04	3.44	2.14
Recycle/product ratio ^h	3.7	3.5	3.4	4.1	3.8	4.2
Drum speed, rpm	16	16	16	16	16	16
Dryer:						
Airflow rate (outlet conditions), m ³ /hour	5,440	5,500	5,050	5,180	5,520	5,050
Air velocity (outlet conditions), m/second	2.71	2.74	2.51	2.58	2.75	2.51
Temperature of fertilizer discharge, °C	90	91	93	94	92	93
Temperature of air discharge, °C	101	106	106	104	104	105
Relative humidity of air discharge, % ^j	10	4	6	7	7	4
Relative humidity of ambient air, %	47	55	76	58	45	45
Temperature of ambient air, °C	31	20	19	19	29	16
Drum speed, rpm	7	7	7	7	7	7
Screened product:						
Maximum particle size, mm	3.35	3.35	3.35	3.35	3.35	3.35
Minimum particle size, mm	1.18	1.18	1.18	1.18	1.18	1.18
pH ^d	7.6	8.0	7.7	7.7	7.6	7.9

Notes for Table 4

- a. Although it was intended to have a low F/P₂O₅ weight ratio in this test run by defluorinating the acid through heating, chemical analyses showed high F/P₂O₅ weight ratios in the feed phosphoric acid and in the screened product.
- b. These rates were calculated by equating all the P₂O₅ flow rates in the plant to the P₂O₅ fed to the preneutralizer.
- c. Period during which slurry was fed to granulator.
- d. As determined by method outlined in Appendix A.
- e. Stoichiometric is defined as the feed rate of ammonia required to bring the preneutralizer slurry from its N/P₂O₅ weight ratio to that of DAP (0.391).
- f. Defined as the screen opening that would retain 50% by weight of the material.
- g. Second temperature denotes the temperature of material spilling over the internal retention dam inside the granulator.
- h. Defined as the weight ratio of measured recycle rate to the calculated production rate.
- i. NA = not available.
- j. Measured at the stack.

Table 5 Results of Chemical Determinations on Samples Taken During Extended Test Runs (wt %)^a

Test	Baseline 7-187	A 7-206	B 7-191	AB 7-212	C 7-197	AC 7-204	BC 7-200	ABC 7-208	Midpts I 7-202	Midpts II 7-210	Midpts III 7-216	B(low F) 7-214	BC(low F) ^b 7-199	C(no H ₂ O) ^c 7-218
Feed acid (IMC, New Wales laboratory):														
Total P ₂ O ₅	39.73	46.99	39.44 ^c	42.68	41.21	39.16	36.55	43.67	41.60	46.30	45.85	41.24	43.11	42.12
Al ₂ O ₃	1.03	1.81	1.10 ^c	1.50	1.30	1.41	1.00	2.05	1.34	1.44	1.33	1.03	1.08	1.14
MgO	0.83	0.90	1.65 ^c	1.71	0.84	0.72	1.52	1.81	1.26	1.35	1.41	1.69	1.85	0.76
Fe ₂ O ₃	0.95	1.06	1.04 ^c	1.08	2.00	1.98	1.82	2.15	1.74	1.64	1.57	1.10	2.04	2.25 ^d
F	1.69	1.22	3.49 ^c	3.03	1.50	1.58	3.26	2.84	2.42	1.72	1.88	1.46	3.12	1.28
H ₂ O Karl Fischer	37.55	26.88	NA ^e	30.45	34.56	37.62	37.95	27.13	32.10	26.52	26.63	33.69	28.86	33.07
Feed acid (indicated)														
Total P ₂ O ₅	39.91	43.31	38.87	42.46	40.28	39.20	39.01	42.05	39.72	42.80	43.82	40.52	40.87	41.29
Al ₂ O ₃ ^g	1.00	1.58	1.12	1.46	1.26	1.35	1.06	1.62	1.24	1.36	1.35	1.05	1.12	1.09
MgO ^g	0.81	0.84	1.67	1.77	0.72	0.74	1.59	1.79	1.27	1.27	1.22	1.68	1.76	0.77
Fe ₂ O ₃ ^g	0.99	1.13	1.05	0.99	1.98	2.00	1.97	2.16	1.72	1.65	1.56	1.11	2.03	2.18
F	1.83	1.95	4.77	5.55	1.85	1.80	4.79	5.49	3.34	3.74	3.83	1.83	5.01	1.86
Scrubber liquor (IMC, Florence Lab.):														
Total N	2.6 ^c	4.2	3.7	3.6	4.2	3.7	3.7	3.7 ^c	3.5	4.7	3.9	3.0	4.0	3.1
Total P ₂ O ₅	40.7 ^c	47.3	41.1	44.9	42.4	41.7	40.1	44.0 ^c	43.8	46.3	46.3	42.1	44.8	40.2
Preneutralizer slurry (IMC, New Wales laboratory):														
Total N	12.87	13.34	12.96	12.63	13.36	11.51	12.27	11.99	12.72	13.1	12.55	12.93	12.51	12.83
Total P ₂ O ₅	41.08	44.61	41.26	42.12	43.50	37.74	39.67	41.43	42.06	44.5	42.28	42.00	40.72	44.27
Granulator discharge (IMC, Florence laboratory):														
Total N	17.6	17.9	17.7	17.9	17.8	17.4	17.4	17.0 ^c	17.2	17.8	17.9	17.7	17.4	18.4
H ₂ O	3.4	3.5	3.5	2.8	3.2	3.5	3.6	3.2 ^c	3.3	3.2	4.2	3.3	3.2	2.6
Dryer discharge (IMC, Florence laboratory):														
Total N	17.7	17.9	18.0	17.9	17.9	17.6	17.5	17.2 ^c	17.4	17.9	18.1	17.9	17.2	18.5
H ₂ O	2.1	2.0	2.4	2.3	2.0	2.1	2.3	2.4 ^c	2.5	NA	2.3	2.1	2.3	1.4
Recycle (IMC, Florence laboratory):														
Total N	17.8	17.7	17.9	17.9	17.8	17.6	17.2	17.0 ^c	17.5	17.8	18.0	17.9	17.01	18.5
H ₂ O	1.9	2.2	2.6	2.3	2.1	2.3	2.4	2.5 ^c	2.4	NA	2.5	2.3	2.4	1.5
Screened product (IMC, New Wales laboratory):ⁱ														
Total N	18.92	18.32	18.42	17.96	18.23	18.15	17.99	17.55	17.81	18.14	18.41	18.12	17.85	18.36
Total P ₂ O ₅	48.25	48.57	46.27	46.86	47.67	47.77	45.83	46.53	47.03	47.51	47.53	46.95	46.28	48.04
Cl P ₂ O ₅	0.44	0.11	0.17	0.02	0.35	1.46	0.05	0.07	0.27	0.03	0.03	0.02	0.07	0.21
Al ₂ O ₃	1.21	1.77	1.33	1.62	1.50	1.65	1.24	1.80	1.47	1.51	1.46	1.21	1.26	1.27
MgO	0.98	0.94	1.98	1.96	0.85	0.91	1.86	1.98	1.50	1.41	1.32	1.95	1.99	0.89
Fe ₂ O ₃	1.20	1.26	1.24	1.10	2.35	2.44	2.31	2.39	2.04	1.83	1.69	1.29	2.30	2.54
F	1.91	1.56	3.38	3.24	1.75	1.88	3.46	3.16	2.72	2.23	2.03	1.64	3.57	1.53
CaO	0.04	0.01	0.05	NA	0.35	NA	NA	0.02	NA	0.02	NA	NA	0.01	0.05
SO ₃	3.41	3.66	3.76	3.50	3.64	3.46	3.26	3.29	3.42	3.42	3.58	5.70	3.54	3.56
Product moisture, % ^j	1.66	1.32	2.60	1.88	1.96	1.46	2.52	1.78	2.44	2.35	2.28	1.80	2.46	0.72

Notes for Table 5

- a. All samples except where noted correspond to the second sampling period of the particular test run.
- b. Although it was intended to have a low F/P₂O₅ weight ratio in this test run by defluorinating the acid through heating, chemical analyses showed high F/P₂O₅ weight ratios in the feed acid and in the screened product.
- c. Analysis carried out on a sample from the first sample period of the test run.
- d. Includes 0.34% of iron in the Fe⁺⁺ state.
- e. NA = not available.
- f. Obtained by averaging results from IMC (New Wales), IMC (Florence), and IFDC laboratories.
- g. Obtained by assuming the weight ratio of this impurity to P₂O₅ is the same as that found in the screened product.
- h. Obtained by assuming the weight ratio of F/P₂O₅ to be as expected with the actual addition of magnesium fluosilicate.
- i. Screened product analysis is expressed on a dry basis.
- j. Free H₂O in product, not included in above product analysis.

Table 6. Chemical Analysis of Water-Insoluble Solids in DAP Samples From Extended Test Runs^a

Test	Baseline 7-187	A 7-206	B 7-191	AB 7-212	C 7-197	AC 7-204	BC 7-200	ABC 7-208	Midpoints I 7-202	Midpoints II 7-210	Midpoints III 7-216	B (Low F) 7-214	BC (Low F) ^b 7-199	C (NoH ₂ O ₂) 7-218
Content, %:														
CaO	0.86	0.38	0.76	0.53	1.03	0.54	0.51	0.41	0.46	0.43	0.45	0.33	0.62	0.31
Al ₂ O ₃	10.83	12.14	9.57	10.79	8.19	7.94	7.22	8.59	9.45	9.03	9.53	8.54	7.34	7.85
F	10.18	7.41	16.21	16.57	7.54	7.28	13.47	11.04	10.84	9.27	10.21	6.99	13.75	6.41
MgO	7.55	6.29	12.49	12.56	6.22	4.93	10.88	9.27	8.96	8.62	9.66	12.58	11.50	5.55
SO ₄	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe ₂ O ₃	9.33	8.02	8.29	8.02	15.72	12.54	14.05	11.66	12.10	10.97	11.48	7.78	14.16	15.68
K ₂ O	0.05	0.06	0.05	0.07	0.08	0.07	0.05	0.04	0.04	0.06	0.05	0.03	0.09	0.04
Total N	5.21	4.69	3.19	3.11	4.86	6.67	3.19	3.32	4.47	3.53	3.60	4.15	3.08	4.73
P ₂ O ₅	33.9	37.4	25.4	27.2	36.7	39.4	28.0	28.8	33.6	31.6	33.5	37.0	29.1	35.5
Na ₂ O	0.20	0.16	0.33	0.34	0.24	0.14	0.22	0.29	0.24	0.27	0.27	0.15	0.33	0.13
SiO ₂	5.5	2.7	8.9	6.7	3.9	4.1	8.2	5.2	6.4	3.8	4.1	4.0	6.7	3.7
H ₂ O of con- stitution	11.8	15.7	13.9	15.1	15.1	10.5	10.1	16.5	13.4	15.1	13.3	18.7	11.7	14.4

a. Water insoluble fractions were obtained by following the procedure outlined in Appendix A.

b. Although it was intended to have a low F/P₂O₅ weight ratio in this test run by defluorinating the acid through heating, chemical analyses showed high F/P₂O₅ weight ratios in the feed phosphoric acid and in the screened product.

Table 7. Water-Insoluble Solid Phases Present in DAP Samples from Extended Test Runs

Test	Baseline 7-187	A 7-206	B 7-191	AB 7-212	C 7-197	AC 7-204	BC 7-200	ABC 7-208	Midpoints I 7-202	Midpoints II 7-210	Midpoints III 7-216	B (Low F) 7-214	BC (Low F) ^a 7-199	C (No H ₂ O ₂) 7-218
Insoluble solid phases present:														
Fe(NH ₄) ₂ (HPO ₄) ₂ F	^b M	^c -	-	-	M	M	-	^d m	-	m	-	-	-	m
M ₃ Al ₂ F ₈ ·2H ₂ O	m	-	M	M	m	-	M	M	-	M	M	m	M	-
MgNH ₄ PO ₄ ·H ₂ O	m	-	-	-	-	-	-	-	-	-	-	m	-	M
AlNH ₄ HPO ₄ F ₂	m	-	m	-	-	-	-	-	-	-	-	m	-	M
MgNH ₄ FO ₄ ·6H ₂ O	-	-	-	-	-	-	-	-	-	-	-	m	^e T	m
(Al,Fe)NH ₄ (HPO ₄) ₂ · 0.5H ₂ O	m	-	m	-	m	m	-	-	-	-	-	-	-	T
Fe(H ₂ PO ₄)·2H ₂ O	T	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe ₃ (PO ₄) ₂ ·8H ₂ O	-	-	-	-	-	-	-	-	-	-	-	-	-	T
Unidentified	T	-	-	-	-	-	-	-	-	-	-	-	-	T
Silica get	T	-	m	m	T	-	m	m	-	m	m	T	m	-
Amorphous	m	M	m	m	M	m	m	M	M	M	M	M	m	M

- a. Although it was intended to have a low F/P₂O₅ weight ratio in this test run by defluorinating the acid through heating, chemical analyses showed high F/P₂O₅ weight ratios in the feed phosphoric acid and in the screened product.
- b. M represents a major occurring phase; at least 40% by weight.
- c. - represents a phase not found in the analyses.
- d. m represents a minor occurring phase; between 10% and 40% by weight.
- e. T represents a phase occurring in trace amounts; less than 10% by weight.

Table 8. Physical Properties of Screened Products From Extended Runs^a

<u>Test</u>	<u>Acid Treatment</u>	<u>Crushing Strength</u> (kg/granule)	<u>Bulk Density</u> (mt/m ³)	<u>Critical Relative Humidity</u> (% RH)	<u>Moisture Absorption^b</u> (mg/cm ²)	<u>Moisture Penetration^b</u> (cm)	<u>Moisture Holding Capacity^b</u> (mg/cm ²)
7-187	Baseline	4.8	0.79	65-75	196	1.8	109
7-206	A	5.2	0.80	65-75	180	1.5	120
7-191	B	3.7	0.85	65-75	204	2.1	97
7-212	AB	5.0	0.82	65-75	209	1.6 ^c	131
7-197	C	4.6	0.78	65-75	206	1.6	129
7-204	AC	4.1	0.82	65-75	193	1.3	149
7-200	BC	4.8	0.84	65-75	190	2.0	95
7-208	ABC	5.4	0.80	65-75	193	1.6	121
7-202	Midpoint I	5.7	0.84	65-75	198	1.6	124
7-210	Midpoint II	5.1	0.85	65-75	169	1.8	94
7-216	Midpoint III	4.7	0.86	65-75	148	1.5	98
7-214	B(low F)	5.2	0.81	65-75	217	2.0 ^c	109
7-199	BC(Low F) ^d	4.2	0.82	65-75	204	1.9	107
7-218	C(no H ₂ O ₂)	3.8	0.83	65-75	204	1.4	146

- a. Measured in accordance with TVA Bulletin 147, (Physical Properties of Fertilizer and Methods for Measuring Them).
- b. Measured after 72 hours at 86°F and 80% relative humidity.
- c. Penetration was not uniform, streaking of moisture through otherwise dry areas.
- d. Although it was intended to have a low F/P₂O₅ weight ratio in this test run by defluorinating the acid through heating, chemical analyses showed high F/P₂O₅ weight ratios in the feed phosphoric acid and in the screened product.

Table 9. Summary of Statistical Analysis of Correlation of Production Variables Versus C.I. P₂O₅ and W.I. Fraction Data

Production variables and interactions			Effect (a,c)					
	C.I. P ₂ O ₅ ^(b)	% W.I. fraction	Al	Mg	Fe	F	P ₂ O ₅	N
Al	0	+	0	0	-	0	0	0
Mg	0	+	0	+	0	+	-	-
Fe	0	+	-	-	+	-	0	+
Al·Mg	-	0	0	0	0	0	0	-
Al·Fe	0	0	0	0	-	0	0	+
Fe·Mg	-	0	0	0	0	0	0	-
Al·Mg·Fe	0	0	0	0	0	0	0	-

a. Effect based on significance at the 90% confidence level.

b. The large coefficient of variation calculated for these correlations probably contributes to the lack of effect calculated for C.I. P₂O₅.

c. - = negative effect; + = positive effect; 0 = insignificant effect.

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TA/84/6 Effects of impurities on production of diammonium phosphate
by M.M. HANDLEY, IM & C, USA

DISCUSSION: Rapporteur S. SWANSTROM, Kemira Oy, Finland

Q - Mr. M. MIYAMOTO, Nissan Chemical Industries, Japan

In table 1, do you have an analysis of sodium oxide Na₂O?

A - The baseline acid contained 0.07% Na₂O.

Q - Mr. K.L. PARKS, Agrico, USA

How is the DAP moisture determined and were the samples ground or unground?

A - The samples were determined immediately upon catching them from the test runs, they were unground samples.

Q - Mr. N. HUMMADI, Jordan Fertilizer Industry, Jordan

What is the water soluble P₂O₅ in the final product (in % of total)?

A - It varied somewhat on each test effort.

Q - What was the F content in the DAP produced, any limit of F in DAP imposed by regulations in USA?

A - There are no regulations on the amount of F in DAP. The DAP reported stoichiometrically to the product.

Q - Any foaming problems in the preneutralizer?

A - We had no foaming problems in the preneutralizer, in the scrubber there were some.

Q - Mr. M. BARLOY, Office Togolais des Phosphates, Togo

What is in your opinion the influence, if any, of Al, Fe and Mg on:

- the plant output, related to the granulation rate
- the caking tendency in the bulk storage.

A - My conclusions are that each of these chemicals basically has effect but on a molecular weight basis they are essentially equal. I would expect from our tests on the high MgO product that at some percentage of MgO we would start having caking problems with final product upon storage. However it is probably higher than the MgO we reached in our tests.

Q - Mr. J.D. CRERAR, Norsk Hydro Fertilizers Ltd, United Kingdom

Hemihydrate process produces phosphoric acid with much lower aluminium level than concentrated dihydrate process acid. Would you speculate on the effect on DAP production using hemihydrate acid?

A - I do not think I can speculate on that, I do not know enough about the acid, I have never run DAP from acid produced by the hemi process.

Q - Mr. K. DALY, Compagnie des Phosphates de Gafsa, Tunisia

Do the impurities Fe₂O₃, Al₂O₃ and MgO have an influence on the particle size of the product coming out of the granulator?

A - Yes. In all cases with all the test efforts we ran with all three impurities, we had granulation problems all the time: I think we solved probably the most effect on granulation of MgO, next with iron and least with aluminium.

Q - Have you tested the effect on the recycle rate?

A - No. The idea was originally to test a chemical, so we tried to maintain constant plant effort all throughout.

Q - Mr. Y. COTONEA, CdF Chimie AZF, France, Mr. G.H.M. CALIS, UKF, Netherlands

Could you confirm that the viscosity of the slurry is better with the high content of magnesium?

A - With the high magnesium runs we had lower viscosity than we did with high aluminium and high iron. But I did not put this on a mole basis, so I am not sure that I can confirm that.

Q - Mr. D. IVELL, Norsk Hydro Fertilizers Ltd, United Kingdom

In the high Al acid tests no more ammonia was added to the granulator than in the other tests. Could not nitrogen grade have been made at the expense of a little higher ammonia loss in the scrubber?

A - No, we actually ran an extra test running much more stoichiometric, trying to get much more ammonia into the preneutralizer and we were unable to. We also overammoniated the granulator. No success.

Q - Mr. J.A. BENES, Uhde GmbH, Germany

Were you, as a result of the tests described here, able to reduce the citrate-insoluble P₂O₅ in DAP product from your new plant in New Wales? If yes, how did you do it?

A - The main thing we found out which reinforced the work we had done was that the temperature and the retention time were the two critical factors along with the fluorine levels, if you have control of that in the preneutralizer. By reducing retention time and holding temperatures as low as possible you still keep the fluidity, we were able to reduce the CI's.

Q - Mr. J.C. ABRAHAMSE, UKF, Netherlands

Your tests were carried out with magnesium fluosilicate and

magnesium sulfate. Did you notice an effect from silicates on production and on product's properties?

A - No we did not. As to the runs that we repeated with magnesium sulfate versus the fluosilicate, we did not see a great deal of difference.

Q - Mr. P. BECKER, COFAZ SA, France

Do you have an explanation why aluminium reduces the granule's porosity?

A - I do not have. I am sure it has to do with the viscosity and the fact that we were really making a MAP along with the DAP with the aluminium runs.