Control of Citrate-Insoluble Phosphate Formation in Ammonium Phosphate Manufacture

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The formation of citrate-insoluble phosphates may be minimized by maintaining a high pH value during ammoniation of wet process phosphoric acid. This principle has proved effective in two large fertilizer plants.

CITRATE-INSOLUBLE PHOSPHATES have been an uncontrollable loss to nearly all ammonium phosphate manufacturers.

Until the following work was carried out, it was not possible to relate the level of citrate-insoluble phosphate to any of the process factors. Investigations at the ammonium phosphate plant at Trail during the 1930's proved that the citrate-insoluble phosphate was not related to the calcium or sulfate content of the citrate-insoluble residues, to the calcium-sulfate ratio in the final product, nor to the solids content of the acid feed. More recently, plant surveys showed that most or all of the citrate-insoluble phosphate was generated in the ammoniation step.

The citrate-solubility test was devised to determine the unreacted rock in ordinary superphosphate. The development of this procedure is summarized by Jacob and Hill (3). The citrate-insoluble phosphate in ammonium phosphates is not rock phosphate; a comparison of the x-ray diffraction data which follow with those of Hecht et al. (2) makes this very clear. By alterations in the temperature or the time of leaching in the citrate-solubility procedure, the citrate-insoluble phosphate in ammonium phosphates derived from wet process phosphoric acid may be reduced to zero. However, because the availability of the citrate-insoluble phosphate in these products is not known, it is assumed to be zero, and the citrate-insoluble phosphate method is used commercially to evaluate ammonium phosphates as well as superphosphates.

Unless otherwise specified, the phosphates referred to are derived from Montana phosphate rock.

Experimental

Ammoniation of Phosphoric Acid. An investigation of this operation disclosed that pure phosphoric acid did not produce any citrate-insoluble matter.

When iron, aluminum, or both were added to the acid, citrate-insoluble phosphate appeared in the 11–48–0 derived therefrom.

Ferric, and especially ferrous, hydroxide added at any stage in the manufacture of 11–48–0 increased the citrate-insoluble phosphate, even if added to the final dried product. Aluminum hydroxide did not have this effect, alone or in the presence of iron hydroxides.

The citrate-insoluble phosphate could be markedly increased by ammoniating the wet process acid to a pH between 0.5 and 2, leaving it at this pH for a time, and then completing the ammoniation. The longer the mix was left at a pH of 0.5 to 2, the higher the citrate-insoluble phosphate (Table I).

These findings indicate that citrate-insoluble compounds form in partially ammoniated phosphoric acid in the pH range 0.5 to 2 in the presence of iron and/or aluminum and that in the critical pH range, the citrate-insoluble phosphate increases with time.

Identification of Citrate-Insoluble Material. Large scale extraction of citrate-soluble matter for the purpose of obtaining citrate-insoluble residues for analysis proved unsatisfactory. To obtain the proper insoluble residues it was necessary to extract 1 gram at a time in the manner set out in the method of analysis.

These residues were found to contain quartz, coal, and an unidentified white material. An average analysis of such residues has no real meaning, but a typical analysis of the citrate-insoluble residue used in our work is shown in Table II. The x-ray diffraction pattern given by this particular sample is given in Table III (Pattern 1).

Various compounds containing iron, aluminum, ammonium, and phosphate were prepared by solution and by fusion methods, in an attempt to obtain a compound which would give the same x-ray diffraction pattern as the residue mentioned above. Materials precipitated from solution gave the desired pattern.

The precipitates were prepared by dissolving monoammonium phosphate in phosphoric acid and then adding ferrous, ferric, or aluminum phosphate in the combination and concentration desired. The purest available reagents were used. Any undissolved material was filtered off. A solution of diammonium phosphate was then used to adjust the pH to the desired level.

The precipitates formed at a pH of 2 or less gave sharp x-ray diffraction patterns (Patterns 2 and 3, Table III). The precipitate giving Pattern 2 has practically the same analysis as the theory for $NH_4H_2PO_4.FePO_4$ and this pattern is the same as that for the citrate-insoluble residue (Pattern 1). Analyses of the various precipitates and melts are given in Table IV.

The precipitates formed at a pH over 2 were presumably amorphous, as they gave no x-ray diffraction pattern. The nitrogen content of these precipitates was lower than any of the other materials studied and the citrate-insoluble content was practically nil.

Precipitates from aluminum ammonium phosphate solutions were clearly not related to the citrate-insoluble phosphate problem.

Infrared absorption measurements confirmed the identity of citrate-insoluble

Table I. Effect of pH and Retention Time on Formation of Citrate-Insoluble Matter

pH	Retention Time, Hours	Citrate-Insoluble P_2O_5 Produced, %
0.5	0.0	0.2[a]
	4	0.4[a]
	6	1.6[a]
	7	4.6[a]
	24	15.8[a]
0.55	2.5	0.6[b]
1.05	2.5	0.3[b]
1.65	2.5	Trace[b]
2.35	2.5	Trace[b]

[a] Partial ammoniation precipitate.
[b] Final 11–48–0.

Table II. Analysis of a Citrate-Insoluble Residue

Conventional		Elementary		
Component	%	Element	%	Mole/kg.
N	5.6	N	5.6	4.0
CaO	1.9	Ca	1.4	0.35
Fe_2O_3	10.3	Fe	7.2	1.29
Al_2O_3	15.1	Al	8.0	2.97
P_2O_5	35.1	P	15.3	4.94
SO_4	0.22	S	0.07	0.22
F	8.9	F	8.9	4.68
SiO_2	7.8	Si	3.6	1.28
C	1.5	C	1.5	[a]

[a] Present as coal.

matter from ammonium phosphate derived from Montana phosphate rock and from Florida phosphate rock, and Compound 2, Table IV.

The complex salt monoammonium phosphate–ferric phosphate is evidently responsible for the x-ray diffraction pattern and the infrared absorption curves of the above citrate-insoluble residues.

The compounds formed by fusion were not in evidence in the citrate-insoluble residue. This point was checked because early work indicated that some citrate-insoluble phosphates might be formed in the fertilizer dryer. It was shown that monoammonium phosphate–ferric phosphate was stable up to 200° C. but that by the time 1000° C. was reached it decomposed to something giving only a single line in the x-ray diffraction pattern.

In producing the monoammonium phosphate–ferric phosphate, both ferrous and ferric salts could be used, but the ferrous salts gave crystalline (and hence citrate-insoluble) salts more readily. Possibly the slow oxidation of ferrous to ferric allows crystallization of the complex salt.

Fluorine is known to play a considerable role in the formation of citrate-insoluble phosphate in fertilizer mixtures (4). Fox and Hill (1) explained this on the basis of fluosilicates present in wet-process acid. However, in the present work no influence by various fluorine-containing compounds on the synthetic precipitates and the citrate solubility was found. Nor did evidence of fluorine bonds show in the infrared absorption spectra of the residue from the fertilizer. Presumably the fluorine is there as an amorphous electrovalent compound. There is no difference in the x-ray diffraction patterns nor in the infrared absorption spectra of the citrate-insoluble residue from 11–48–0 from Florida rock (1% F) or from 11–48–0 from Montana rock (3% F).

Consecutive citrate solubility determinations on Compound 4 (Table IV) indicated 35% citrate-insoluble phosphate in the original precipitate, 18% (based on the original sample) in the second, and 13% in the third determination. This, together with the preceding item, supports the thought that solubility or nonsolubility in the citrate reagent is dependent on particle size. Very fine crystallites of the complex salt might not give an x-ray pattern and would be readily soluble. Opposed to this idea is the difference in analysis of the crystalline and noncrystalline materials.

Application to Plant Operation. According to the above findings, citrate insolubility might be minimized in the plant by removing the iron from phosphoric acid or by avoiding acid conditions in the ammoniator. The latter course is the only one that could be considered from a practical point of view.

An opportunity to test the thesis was presented when a new ammonium phosphate plant was being brought into production, in which the ammoniation was carried out by series and by parallel ammoniation.

SERIES AMMONIATION. Most of the ammoniation was carried out in the first agitator in a three-agitator cascade, the balance was carried out in the second agitator, and any final adjustments were made in the third. In this test, the first agitator was highly acid, as customary, and the remaining two were maintained neutral to bromcresol green indicator, a pH of about 4 to 5.

The 11–48–0 so produced contained 0.4% citrate-insoluble phosphate.

PARALLEL AMMONIATION. Full ammoniation was carried out in the first two agitators simultaneously and any final adjustments were made on the combined flows in the third agitator. All agitators were maintained neutral to bromcresol green.

The 11–48–0 so produced contained only traces of citrate-insoluble phosphate.

In the older plant units, when converted from series to parallel ammoniation, citrate-insoluble phosphate was reduced from an average of 0.5% to an average of around 0.1%.

These changes have had no detectable effect on the water solubility of the phosphate compounds.

Literature Cited

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(2) Hecht, W. J., Jr., Worthington, E. A., Crittendon, E. D., Northrup, M. A., Ind. Eng. Chem. 44, 1119–23 (1952).
(3) Jacob, K. D., Hill, W. L., "Soil and Fertilizer Phosphorus," W. H. Pierre, H. G. Norman, eds., Chap. X, Academic Press, New York, 1953.
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Table III. X-Ray Diffraction Data

Pattern 1		Pattern 2		Pattern 3		Pattern 4		Pattern 5	
d/nA	I	d/nA	I	d/nA	I	d/nA	I	d/nA	I
...	...	...	...	8.50	80	5.95	100	5.90	100
7.80	60	7.80	60	7.80	100	5.20	10	4.90	80
...	...	...	...	6.60	80	4.02	90	3.95	80
6.30	70	6.30	90	6.20	100	3.49	5	...	...
...	...	...	...	4.10	15	3.03	90	2.98	90
...	...	...	...	3.90	5	2.85	5	...	...
...	...	...	...	3.75	5	2.75	10	...	...
3.59	5	3.60	5	3.58	25	2.65	5	...	...
3.35[a]	100	...	...	...	...	2.47	5	...	...
3.24	15	3.28	10	3.25	15	2.34	5	...	...
3.12	80	3.12	90	3.10	100	2.09	5	...	...
2.98	80	2.98	90	2.95	100	2.01	5	...	...
2.76	5	2.74	5	...	...	...	...	...	...
2.69	60	2.69	60	2.67	40	...	...	...	...
2.56	5	2.56	5	2.55	5	...	...	...	...
2.44	5	2.44	5	2.42	10	...	...	...	...
2.32	5	2.33	5	2.30	10	...	...	...	...
2.24	5	2.24	5	2.22	10	...	...	...	...
2.14	5	2.14	5	2.14	5	...	...	...	...

[a] Quartz line.

Table IV. Table of Analyses

Material	Analysis, Weight %					X.R.D. Pattern No.
	N	P_2O_5	C. I. P_2O_5	Al_2O_3	Fe_2O_3	
Citrate-insoluble matter from 11–48–0	5.6	35.1	?	15.1	10.3	1
Iron ammonium phosphate precipitate, crystalline	5.3	53.3	38.8	0	28.8	2
Iron ammonium phosphate precipitate, amorphous	3.4	49.8	0.1	0	29.4	...
Iron aluminum ammonium phosphate precipitate, crystalline	4.9	55.7	34.9	11.5	14.9	3
Iron ammonium phosphate melt	5.5	45.2	37.2	0	30.0	4
Iron aluminum ammonium phosphate melt	6.0	52.8	37.0	7.2	19.5	5
$NH_4H_2PO_4 \cdot FePO_4$, calculated	5.3	53.5	...	...	30.0	...