

PHOSPHATE REVERSION

Effect of Sodium Salts on Formation of Citrate-Insoluble Phosphorus Pentoxide in Mixed Fertilizers

ROBERT W. WAY¹ and ELMER L. NELSON

Nitrogen Division, Allied Chemical & Dye Corp., Hopewell, Va.

Inclusions of small amounts of inorganic sodium salts in bench scale preparations of nitrogen-phosphate and nitrogen-phosphate-potash fertilizers inhibit the formation of citrate-insoluble phosphorus pentoxide. The effect is more apparent when the sodium salt is added to phosphate rock before acidulation than when it is added to the superphosphate just prior to ammoniation.

SEVERAL FACTORS influence the degree of reversion of phosphorus pentoxide from a soluble to an insoluble form in the manufacture of some types of fertilizers. Numerous studies have been reported on the effects of rate of ammoniation (6-8, 17), increased temperature during ammoniation (3, 17), increased temperature during storage (4, 5, 7), high moisture content during storage at increased temperature (5, 7, 8), and the presence of fluorine (9, 10).

The effect of fluorine on reversion was the subject of a study conducted by this laboratory and reported by Datin *et al.* (2). Early in the investigation various inorganic fluoride salts were used as a source of fluorine. It was found repeatedly that the addition of sodium fluoride to synthetically prepared superphosphates resulted in fertilizer products that

¹ Present address, Allied Chemical & Dye Corp., La Platte, Neb.

contained less unavailable phosphorus pentoxide than similarly prepared synthetic fertilizers with added calcium or potassium fluoride. Further preliminary work showed that salts of sodium—for example, sodium nitrate and sodium chloride—added with or without calcium fluoride to synthetically prepared superphosphates were effective in preventing reversion of the phosphorus pentoxide. This desirable effect attributed to sodium seemed worthy of further investigation, for if the inclusion of sodium as a relatively inexpensive inorganic salt resulted in a fertilizer that had a greater amount of available phosphorus pentoxide, the profit realized from the increased available phosphorus pentoxide could conceivably be greater than the cost of the added sodium salt.

Three series of studies were conducted. The initial series included four sets of complete fertilizers prepared on a bench

scale, with various amounts of sodium added as sodium nitrate to the mixtures of superphosphate, ammonium sulfate, potassium chloride, dolomite, and sand filler mixture just prior to ammoniation. Concentrated superphosphate (triple superphosphate) was added when necessary in the preparation of the high analysis fertilizers. The second series comprised bench scale preparation of four sets of nitrogen-phosphorus fertilizers. Various amounts of sodium nitrate, sodium chloride, sodium sulfate, and sodium fluoride were added to superphosphate just prior to ammoniation. In the final series various amounts of the same four sodium salts were added to batches of Florida phosphate rock prior to sulfuric acid acidulation and the resulting special superphosphates were subsequently ammoniated. Pertinent data obtained relating to the three series of studies are summarized.

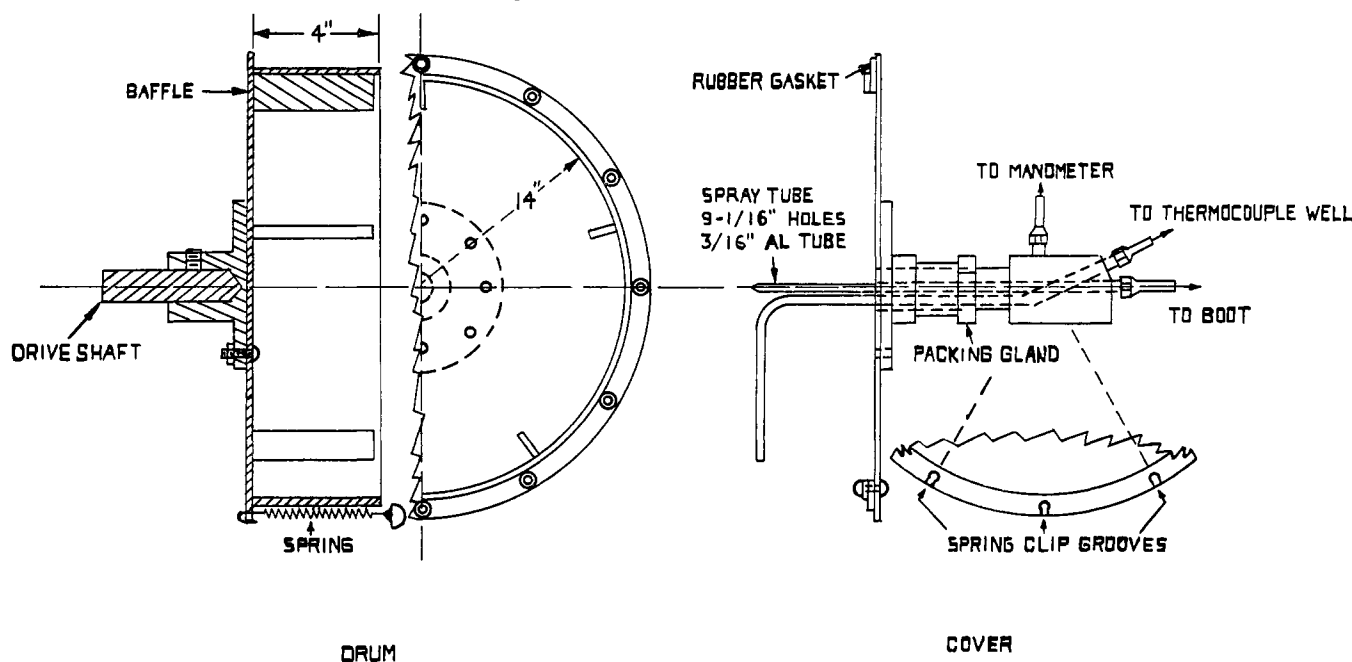


Table I. Effect of Preammiation Addition of Sodium as Sodium Nitrate on Phosphorus Pentoxide Availability in Nitrogen-Phosphorus-Potassium Fertilizers

Fertilizer No.	Na as NaNO ₃ Added, % of Fertilizer ^a	P ₂ O ₅ , Wt. %, Dry Basis After 30 Days, 50° C. Storage			P ₂ O ₅ , Wt. %, Dry Basis After Addl. 30 Days, 80° C. Storage		
		Total	Citrate-ins.	% P ₂ O ₅ Unavailable ^b	Total	Citrate-ins.	% P ₂ O ₅ Unavailable ^b
6-9-6 Fertilizers, Ammoniation Rate 7 Lb. NH ₃ /Unit Total P ₂ O ₅							
NPK1	0.00	9.30	0.60	6.46	9.47	0.69	7.28
NPK2	0.09	9.20	0.60	6.52	9.25	0.66	7.14
NPK3	0.19	9.25	0.60	6.49	9.25	0.63	6.82
NPK4	0.27	9.30	0.59	6.30	9.23	0.63	6.84
NPK5	0.54	9.29	0.58	6.20	9.22	0.65	7.05
NPK6	1.08	9.12	0.60	6.52	9.18	0.60	6.54
10-11-10 Fertilizers, Ammoniation Rate 7 Lb. NH ₃ /Unit Total P ₂ O ₅							
NPK8	0.00	11.50	0.60	5.22	11.63	0.88	7.56
NPK9	0.15	11.38	0.56	4.88	11.43	0.74	6.48
NPK10	0.30	11.40	0.60	5.25	11.75	0.76	6.47
NPK11	0.60	11.39	0.56	4.85	11.73	0.69	5.88
NPK12	1.00	11.65	0.54	4.65	11.50	0.72	6.27
6-13-6 Fertilizers, Ammoniation Rate 4.75 Lb. NH ₃ /Unit Total P ₂ O ₅							
NPK13	0.00	13.80	1.03	7.48	14.02	2.73	19.43
NPK14	0.09	13.58	1.02	7.52	13.95	2.86	20.53
NPK15	0.19	13.55	1.02	7.53	13.93	2.64	19.00
NPK16	0.27	13.80	1.06	7.68	13.95	2.42	17.35
NPK17	0.54	13.00	0.88	6.77	13.33	1.74	13.02
NPK18	1.08	13.63	0.92	6.74	13.88	1.49	10.70
8-17-16 Fertilizers, Ammoniation Rate 4.9 Lb. NH ₃ /Unit Total P ₂ O ₅							
NPK19	0.00	17.52	0.58	3.32	17.13	1.56	9.14
NPK20	0.09	17.45	0.59	3.38	17.20	1.54	8.95
NPK21	0.19	17.78	0.55	3.09	17.60	1.54	8.75
NPK22	0.27	17.83	0.52	2.91	17.78	1.44	8.11
NPK23	0.54	17.85	0.51	2.86	17.85	1.23	6.89
NPK24	1.08	17.88	0.55	2.08	17.45	1.05	6.05

^a c.p. grade.

$$^b \text{ \% of P}_2\text{O}_5 \text{ unavailable} = \frac{\text{citrate-ins. P}_2\text{O}_5}{\text{total P}_2\text{O}_5} \times 100.$$

Table II. Effect of Preammiation Addition of Sodium, as Sodium Nitrate, Sodium Chloride, Sodium Sulfate, and Sodium Fluoride, on Phosphorus Pentoxide Availability in Nitrogen-Phosphorus Fertilizers

Fertilizer No.	Sodium		P ₂ O ₅ , Wt. %, Dry Basis, After 30-Day Storage at 80° C.		% P ₂ O ₅ Unavailable ^b	Moisture, %
	% of fertilizer	Added as	Total	Citrate-ins.		
NP1	0.0	NaNO ₃ ^a	14.65	3.13	21.35	9.3
NP2	1.0	NaNO ₃	15.08	1.43	9.51	9.3
NP3	2.0	NaNO ₃	15.75	1.38	8.77	9.4
NP4	4.0	NaNO ₃	14.70	1.11	7.52	10.7
NP5	0.0	NaCl ¹	14.95	3.10	20.76	10.0
NP6	1.0	NaCl	14.98	1.62	10.80	10.1
NP7	2.0	NaCl	14.30	1.33	9.36	10.0
NP8	4.0	NaCl	14.95	1.27	8.49	10.4
NP9	0.0	Na ₂ SO ₄ ^a	14.83	2.25	18.50	8.8
NP10	1.0	Na ₂ SO ₄	14.85	1.60	11.50	8.7
NP11	2.0	Na ₂ SO ₄	14.88	1.54	10.36	8.4
NP12	4.0	Na ₂ SO ₄	15.28	1.36	8.86	8.8
NP13	0.0	NaF ^a	14.68	2.63	18.00	10.1
NP14	1.0	NaF	14.73	1.59	10.75	9.9
NP15	2.0	NaF	14.68	1.28	8.70	10.2
NP16	4.0	NaF	14.93	1.11	7.40	10.7

^a c.p. grade, anhydrous.

$$^b \text{ \% of P}_2\text{O}_5 \text{ unavailable} = \frac{\text{citrate-ins. P}_2\text{O}_5}{\text{total P}_2\text{O}_5} \times 100.$$

monia to phosphorus pentoxide, within each set, utilizing the apparatus described by Datin *et al.* (2) and shown in Figure 1. Nitrogen solution composed of 21.7% ammonia, 65% ammonium nitrate, and 13.3% water was added at a rate of 250 ml. per minute. The ammoniated mixtures were tumbled an additional 3 minutes to ensure complete ammonia absorption. Portions of the products were placed in jars, sealed, and stored at 50° C. for 30 days, and at 80° C. for 30 days longer.

The products after storage at 50° C. for 30 days and 80° C. for 30 days were dried at 50° C. for 3 hours, ground in a Mikro-Samplmill fitted with a 0.020-inch perforated screen, then analyzed for total and citrate-insoluble phosphorus pentoxide by the AOAC procedures (7). The results of analyses are given in Table I.

Nitrogen-Phosphorus Fertilizers

Preammiation Addition of Sodium Salts

Four sets of nitrogen-phosphorus fertilizers in 2-kg. size batches were prepared from ordinary superphosphate containing 22.3% total phosphorus pentoxide, nitrogen solution containing 21.7% ammonia, 65% ammonium nitrate, and 13.3% water, sand filler, water to bring the total moisture content

Nitrogen-Phosphorus-Potassium Fertilizers

Two - kilogram batches of 6-9-6, 10-11-10, 6-13-6, and 8-17-16 fertilizers were prepared from ordinary superphosphate, commercial grade potassium

chloride, dolomite, ammonium sulfate, sand filler, and various amounts of sodium nitrate to increase the sodium content from 0 to 1%. Triple superphosphate was used in the preparation of the 10-11-10 and 8-17-16 fertilizers to yield the desired phosphorus pentoxide content. The appropriate mixtures were ammoniated at constant ratios of am-

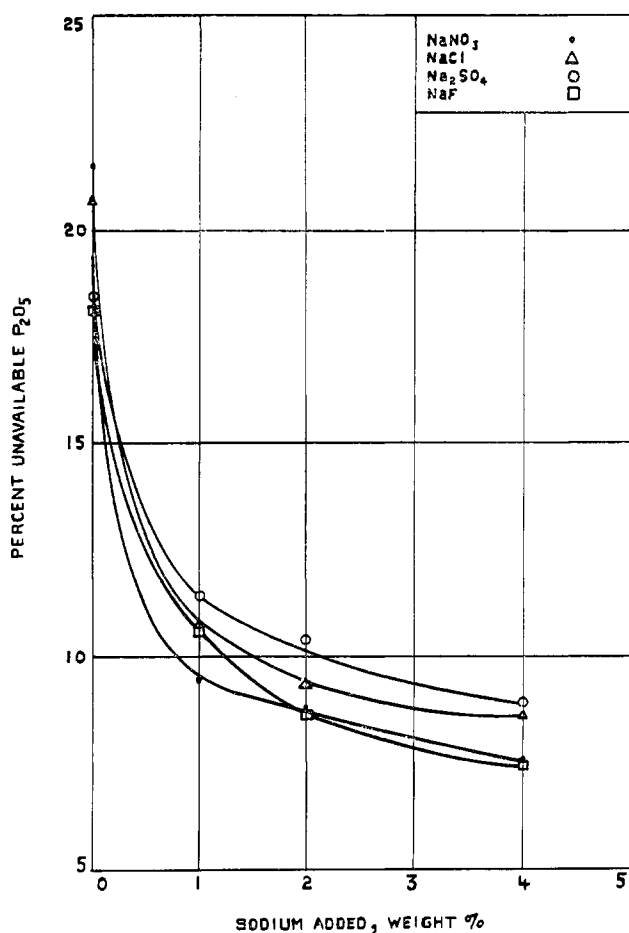


Figure 2. Effect of preammoniation addition of sodium salts on phosphorus pentoxide availability

to 10% by weight, and various amounts of sodium nitrate, sodium chloride, sodium sulfate, and sodium fluoride to yield 0 to 4% sodium in the product. These products were about 9-13-0 formulation. Ammoniation, at the severe rate of 7 pounds of ammonia per unit of total phosphorus pentoxide for all preparations, was accomplished by the same procedure utilized in the initial N-P-K series. Portions of the ammoniated products were placed in jars, sealed, and stored at 80° C. for 30 days.

Portions of the products after storage were dried at 50° C. for about 3 hours, ground in a Mikro-Samplmill fitted with a 0.020-inch perforated screen, then analyzed for total and citrate-insoluble phosphorus pentoxide by the AOAC

procedures (7). Moisture contents of the remaining portions of products after storage were determined by the AOAC procedure (7), which is merely the measurement of the loss in weight after drying in an oven at 100° C. for 2 hours. Results are summarized in Table II. Figure 2 compares graphically the effect of various amounts of the four sodium salts on the availability of the phosphorus pentoxide.

Preammoniation Addition of Sodium Salts

Addition of sodium to rock phosphate prior to acidulation was considered worthy of investigation at this point in the study. A preliminary investigation was conducted.

Two 30-pound batches of superphos-

phates were prepared from Florida phosphate rock and sulfuric acid of 60% concentration by weight. One batch contained no added sodium, whereas the second batch contained 1.7% sodium as sodium nitrate added to the rock phosphate prior to acidulation. The weight ratio of 100% sulfuric acid to phosphate rock was 0.60.

The acidulator was a stainless steel ribbon mixer, shown in Figure 3. The appropriate amount of phosphate rock or phosphate rock and sodium nitrate was placed in the mixer, then the sulfuric acid, preheated to 85° C., was poured into the tumbling mixture. After 1 minute of mixing the frothy mass was dumped into the denning tray, and denned for 18 hours at 100° C.

Portions of the denned batches of superphosphate were treated further in the following manner: Sufficient quantities were taken so that products amounting to 2 kg. were obtained when sand filler, water (to bring the percentage to 10% by weight in the final product), and ammoniating solution were added. The nitrogen solution contained 21.7% ammonia, 65% ammonium nitrate, and 13.3% water. Ammoniations were carried out at the severe rate of 7 pounds of ammonia per unit of total phosphorus pentoxide with the apparatus shown in Figure 1, in the manner previously described. The formulas of the fertilizers thus prepared were about 8-12-0. A portion of the batch prepared without added sodium was similarly ammoniated and sodium was added as sodium nitrate just prior to ammoniation. The amount of sodium in this preparation was 1.1%, equal to the sodium content of the product prepared from superphosphate to which sodium nitrate was added before acidulation.

Each of the ammoniated products was divided into two equal portions. Determinations of total and citrate-insoluble phosphorus pentoxide were run by AOAC procedures (7) on dried (4 hours at 50° C.) and ground (Mikro-Samplmill with 0.020-inch perforated screen) portions of the products immediately after ammoniation. The other portions were placed in jars, sealed, and stored at 80° C. for 30 days. The stored products,

Table III. Effect of Preammoniation Addition of Sodium as Sodium Nitrate on Phosphorus Pentoxide Availability, in Nitrogen-Phosphorus Fertilizers Prepared with Florida Phosphate Rock^a

Fertilizer No.	NaNO ₃ ^b Added	Na Added, % of Product	P ₂ O ₅ , Wt. %, Dry Basis					
			After Ammoniation			After Storage, 30 Days, 80° C.		% of P ₂ O ₅ Unavailable ^c
			Total	Citrate-ins.	Unavailable ^c	Total	Citrate-ins.	
NP17	None	0.0	13.40	0.35	2.62	13.48	1.62	12.02
NP18	Before acidulation	1.1	11.60	0.06	0.48	12.50	0.11	0.84
NP19	Before ammoniation	1.1	12.73	0.31	2.43	14.03	1.29	9.21

^a Phosphate rock contained 34.4% total P₂O₅ (dry basis). Superphosphate prepared from this, containing no added Na, contained 19.15% total P₂O₅, 5.3% unavailable. Superphosphate prepared with Na added before acidulation contained 17.45% total P₂O₅, 4.0% unavailable.

^b c.p. grade.

^c % of P₂O₅ unavailable = $\frac{\text{citrate-ins. P}_2\text{O}_5}{\text{total P}_2\text{O}_5} \times 100$.

Table IV. Effect of Preacidulation Addition of Sodium, as Sodium Nitrate, Sodium Chloride, Sodium Sulfate, and Sodium Fluoride, on Phosphorus Pentoxide Availability in Nitrogen-Phosphorus Fertilizers, Prepared with Florida Phosphate Rock^a

Fertilizer No.	Sodium		P ₂ O ₅ , Wt. %, Dry Basis, After Ammoniation		% P ₂ O ₅ Unavailable ^b	P ₂ O ₅ , Wt. %, Dry Basis, After Storage 30 Days, 80° C.		% P ₂ O ₅ Unavailable ^b
	% of fertilizer	Added as	Total	Citrate-ins.		Total	Citrate-ins.	
NP20	0.00	NaNO ₃ ^c	14.71	1.02	6.93	15.12	3.04	20.45
NP21	0.30	NaNO ₃				14.94	2.34	16.00
NP22	0.60	NaNO ₃	13.96	0.13	0.93	14.82	0.89	6.05
NP23	0.90	NaNO ₃				14.22	0.22	1.50
NP24	1.26	NaNO ₃				14.47	0.14	0.94
NP25	1.70	NaNO ₃	13.76	0.06	0.44	14.82	0.08	0.55
NP26	0.00	NaCl ^c	14.06	0.56	3.98	14.49	2.00	13.83
NP27	0.29	NaCl				14.39	2.08	14.50
NP28	0.58	NaCl	13.36	0.22	1.65	14.16	0.92	6.46
NP29	0.94	NaCl				13.72	0.26	1.90
NP30	1.23	NaCl				13.74	0.14	0.95
NP31	1.67	NaCl	12.96	0.15	1.16	13.99	0.19	1.35
NP32	0.00	Na ₂ SO ₄ ^c	13.06	0.22	1.69	14.27	1.82	12.80
NP33	0.29	Na ₂ SO ₄				14.09	2.05	14.58
NP34	0.58	Na ₂ SO ₄	13.61	0.29	2.13	14.59	1.35	9.23
NP35	0.94	Na ₂ SO ₄				14.32	0.35	2.48
NP36	1.23	Na ₂ SO ₄				14.09	0.14	1.00
NP37	1.67	Na ₂ SO ₄	12.68	0.03	0.24	13.74	0.10	0.77
NP38	0.00	NaF ^b	13.19	0.13	0.98	14.54	1.56	10.75
NP39	0.29	NaF				14.74	1.40	9.47
NP40	0.58	NaF	13.74	0.25	1.82	14.94	2.40	16.08
NP41	0.94	NaF				14.69	1.18	8.00
NP42	1.23	NaF				14.59	0.64	4.36
NP43	1.67	NaF	13.28	0.34	2.56	14.72	0.42	2.82

^a Phosphate rock contained 34.4% total P₂O₅ (dry basis).

^b c.p. grade, anhydrous.

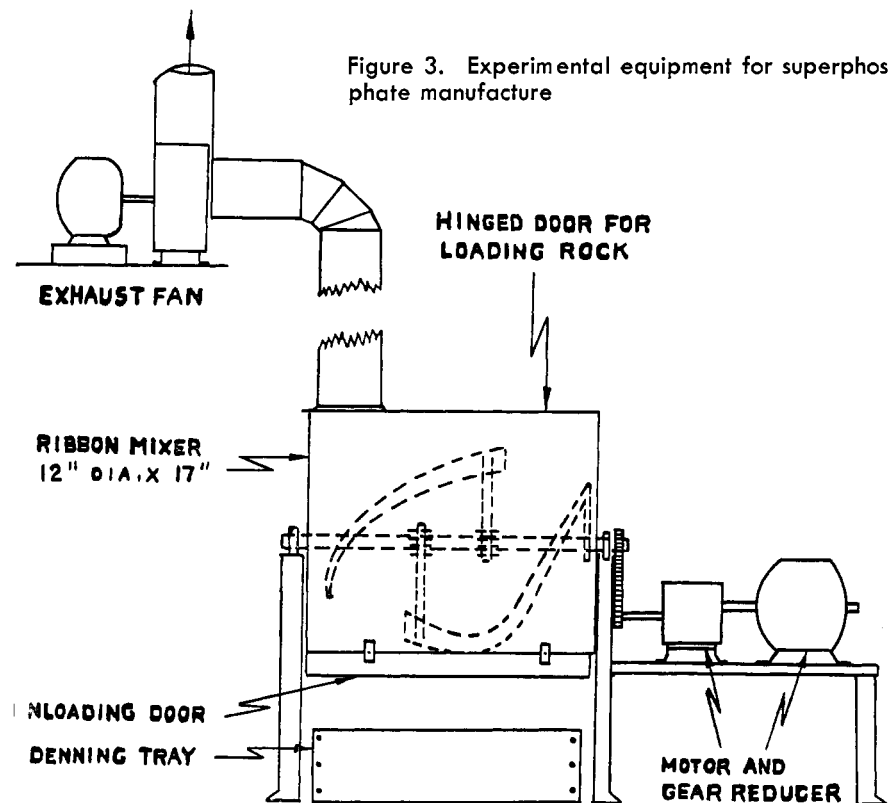
^c % of P₂O₅ unavailable = $\frac{\text{citrate-ins. P}_2\text{O}_5}{\text{total P}_2\text{O}_5} \times 100$.

upon removal, were similarly dried, ground, and analyzed for total and citrate-insoluble phosphorus pentoxide by the AOAC procedures (7). The results are given in Table III.

A more extensive investigation was conducted on the basis of the very favorable results obtained in the preliminary study. Four sets of superphosphates were prepared in 33-pound batches from Florida phosphate rock, and sulfuric acid of 60% concentration by weight. Sodium nitrate, sodium chloride, sodium sulfate, and sodium fluoride were added to vary the percentage of sodium in the superphosphate from 0 to 2.3%. Sand filler was used to adjust the total weights of the mixtures to 33 pounds. A typical mixture included 15 pounds of phosphate rock, 15 pounds of 60% sulfuric acid, 2.80 pounds of sodium nitrate, and 0.20 pound of sand filler. On this basis the weight ratio of 100% sulfuric acid to phosphate rock was 0.60, the same as used in the preliminary investigation. The acidulation procedure was also identical in all respects to that used in the preliminary investigation. However, denning of the superphosphates was done at 85° C. for 20 hours. Two-kilogram batches of fertilizer having an approximate formula of 9-14-0 were prepared from portions of the superphosphates, sand filler, water (to bring the percentage to 10% by weight in the final product), and nitrogen solution of the same composition used in all previous

ammoniations of this study. Ammoniations were carried out at the same severe rate of 7 pounds of ammonia per unit of total phosphorus pentoxide in the apparatus shown in Figure 1 in the manner described previously.

Each of the ammoniated products was divided into two equal parts, one for analysis and one for the storage test. Immediately after ammoniation the analytical portions of three of the six products in each set were dried for 3



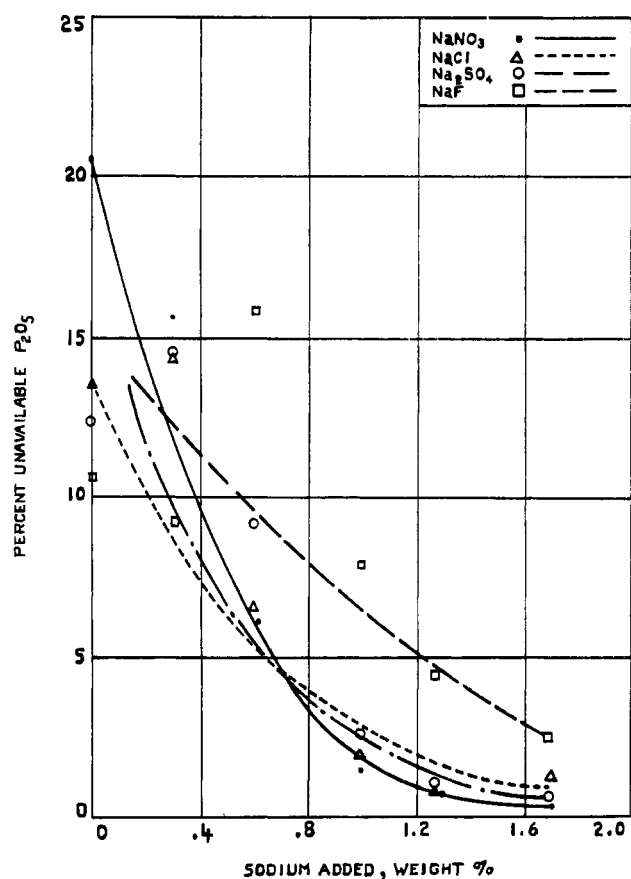


Figure 4. Effect of preacidulation addition of sodium salts on phosphorus pentoxide availability

hours at 50°C., ground in the Mikro-Samplmill to pass the 0.020-inch perforated screen, then analyzed for total and citrate-insoluble phosphorus pentoxide by the AOAC procedures (7). The remaining portions were placed in jars, sealed, and stored at 80°C. for 30 days. After storage, portions of the products were dried, ground, and analyzed for total and citrate-insoluble phosphorus pentoxide in the manner just described. The results are given in Table IV. Figure 4 compares graphically the effect of various amounts of the four sodium salts on availability of the phosphorus pentoxide.

Discussion

The results obtained in this study showed clearly that the inclusion of a small amount of sodium decreased reversion of the phosphorus pentoxide. The effect was more apparent when the sodium was added to the phosphate rock at the preacidulation stage than when it was added to the superphosphate at the preammoniation stage.

Conditions that favor phosphorus pentoxide reversion—severe ammoniation rate, high moisture content, and high storage temperature—prevailed during the preparation of the fertilizers. Under these conditions the reversion was high in the preparations containing no added sodium, and the reversion inhibition effect was markedly shown as the sodium content increased.

The addition of 1% sodium seemed to produce the optimum desired effect. Benefits per unit of sodium added decrease above this concentration. For example, when sodium nitrate was added to phosphate rock before acidulation, with subsequent ammoniation and storage (Table IV, last column), the unavailable phosphorus pentoxide amounted to 20.45% with no added sodium nitrate; the unavailable phosphorus pentoxide with 0.96% sodium added amounted to 15.0%, a decrease in unavailable phosphorus pentoxide of 18.95%; and the unavailable phosphorus pentoxide with 1.70% sodium added amounted to 0.55%, a decrease of only 0.95% unavailable phosphorus pentoxide for an additional 0.74%

Table V. Citrate-Insoluble Phosphorus Pentoxide Content of Residues After Removal of Added Sodium

Fertilizer No.	Citrate-Insoluble P ₂ O ₅ , Wt. %	% of P ₂ O ₅ Unavailable ^a
NP1	2.50	20.54
NP2	1.52	12.16
NP3	1.16	8.62
NP4	0.80	6.26

^a Calculated on basis of total P₂O₅. Water-soluble P₂O₅, 12.17, 12.50, 13.45, and 12.78% for NP1, NP2, NP3, and NP4, respectively.

$$\frac{\text{Unavailable P}_2\text{O}_5 = \frac{\text{citrate-ins. P}_2\text{O}_5}{\text{total P}_2\text{O}_5 - \text{water-sol. P}_2\text{O}_5} \times 100$$

sodium. The inclusion of a sodium salt in actual fertilizer manufacture would involve considerations of cost and handling as related to the increase in available phosphorus pentoxide derived from the added sodium. This aspect is not considered in this report.

The manner in which the added sodium inhibits reversion of the phosphorus pentoxide has not been established. The study of this phenomenon is on the agenda of projects in this laboratory.

A question may be raised concerning the possible effect of the presence of this amount of sodium on the AOAC citrate-insolubility test. It was established in the following manner that the presence of as much as 4% sodium did not affect the AOAC citrate-insoluble method: One-gram samples of each of the four fertilizers of the set to which sodium nitrate was added to give 0, 1, 2, and 4% sodium (Table II, NP1, NP2, NP3, and NP4) were stirred with 100 ml. of water at 65°C. for 1 hour. Analyses of the filtrates indicated complete recovery of the added sodium. Citrate-insoluble phosphorus pentoxide determinations run on the residues showed the same effect on phosphorus pentoxide availability as in the original samples. Results are recorded in Table V.

Acknowledgment

The authors wish to thank Harvey B. Baird, Jr., for the assistance given by him in preparation and analysis of the various fertilizer products in this study.

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Received for review September 17, 1953. Accepted April 5, 1954. Presented before the Division of Fertilizer and Soil Chemistry, Symposium on Fertilizer Technology, at the 124th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.