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Solubilities in the System Magnesium Oxide-Ammonia-Orthophosphoric Acid-Pyrophosphoric Acid-Water at 25 °C

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Measurements were made of solubilities in the system $\text{MgO-NH}_3\text{-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$ at 25 °C. The maximum solubility of MgO was 0.16% at pH 5.30 but only 0.01% at pH 6.11. The addition of ammonium triphosphate corresponding to 13% of the total P_2O_5 (40-42%) had a negligible effect on the solubility of magnesium in the system. However, the solubility of MgO in ammonium polyphosphate solutions will increase from 0.02 to 1.2% when the fluorine level increases from 0 to 2.7%. Thus, magnesium contents above 0.02% MgO which can be obtained in liquid fertilizers appear to be mainly due to a fluoride complex; the presence of adequate fluorine can effectively increase the "saturation" limit of the MgO impurity above the level that is likely to be encountered in commercial wet-process phosphoric acids.

The most troublesome impurity in ammonium polyphosphate fluid fertilizers prepared from wet-process phosphoric acid is magnesium. It precipitates both as complex phosphate salts (Frazier et al., 1972, 1966) in otherwise clear liquid fertilizers and as gels and crystalline solids in suspensions, thereby altering grade and increasing the viscosity to unacceptably high values. Whereas the solubility of magnesium in ammonium polyphosphate liquids is significant in the absence of fluoride, liquids containing a limited quantity of fluoride ions have been shown to solubilize only ~0.01% MgO (Frazier et al., 1972). Consequently, a trend in liquid fertilizer research has been toward reducing the fluoride content to a very low level in wet-process acid prior to production of the liquid fertilizers. However, in the absence of fluorine, no quantitative limits have been determined for the solubility of magnesium in ammonium polyphosphate liquids. The results obtained from experimental and commercial fertilizer solutions in which $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7\cdot 4\text{H}_2\text{O}$ had precipitated are erratic because of the variable fluoride values encountered. Also, it has been theorized that triphosphate will sequester magnesium, but the content of triphosphate varies so greatly in high polyphosphate

liquid fertilizers that if the effect is real, the saturation limit of magnesium would be governed more by this component than by any other factor. The answers to these questions required a study of the ammonium portion of the phase system $\text{MgO-NH}_3\text{-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$ at 25 °C. The significant results are now available for presenting the solubility diagram in the region of interest in fluid fertilizer technology.

EXPERIMENTAL SECTION

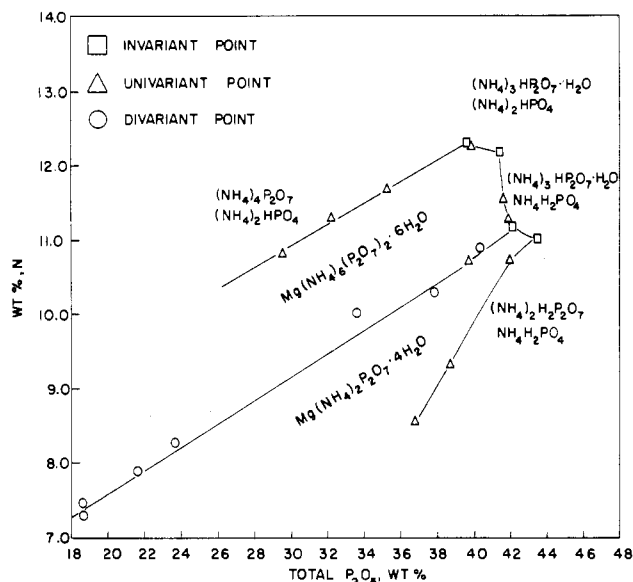
For the study of this five-component system, $\text{MgO-NH}_3\text{-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$, equilibrium mixtures were prepared from recrystallized $(\text{NH}_4)_3\text{HP}_2\text{O}_7\cdot\text{H}_2\text{O}$, reagent $\text{NH}_4\text{H}_2\text{PO}_4$, NH_4OH , and H_3PO_4 . The water-soluble salt, $\text{Mg}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2\cdot 6\text{H}_2\text{O}$, was prepared as the magnesium source. The initial solutions were adjusted to obtain the invariant-point solutions with which three ammonium phosphates and one magnesium ammonium phosphate, or two ammonium phosphates and two magnesium ammonium phosphates, were in equilibrium. The solutions were readjusted periodically so that the desired solid phases finally persisted in well-crystallized euhedral form, after which the mixtures were rotated in a water bath at 25.0 ± 0.1 °C for 3 weeks to ensure equilibrium. The equilibrated liquid phases then were sampled for analysis, and the solid phases were examined microscopically to confirm that the desired phases (Frazier et al., 1972, 1966) had been present throughout the entire equilibration period. The

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Table I. The System MgO-NH₃-H₃PO₄-H₄P₂O₇-H₂O at 25 °C

composition of liquid phase				pH	P ₂ O ₅ as % total P ₂ O ₅	equilibrium solid phase ^a
N	total P ₂ O ₅	ortho-P ₂ O ₅	MgO			
7.48	18.7	13.8	0.02	8.81	26	MgN ₆ + MgN ₂
7.32	18.8	12.9	0.02	8.16	31	MgN ₆ + MgN ₂
7.92	21.6	14.9	0.02	7.66	31	MgN ₆ + MgN ₂
8.29	23.6	15.6	0.02	7.41	34	MgN ₆ + MgN ₂
10.82	29.5	14.2	0.01	7.39	52	N ₄ P ₂ + N ₂ P + MgN ₆
11.31	32.1	14.1	0.01	7.00	56	N ₄ P ₂ + N ₂ P + MgN ₆
11.68	35.3	14.2	0.01	6.56	60	N ₄ P ₂ + N ₂ P + MgN ₆
12.33	39.6	14.4	0.01	6.30	64	N ₄ P ₂ + N ₂ P + MgN ₆ + N ₃ P ₂
10.07	33.6	18.1	0.03	6.19	46	MgN ₆ + MgN ₂
12.28	39.7	14.2	0.01	6.11	64	N ₃ P ₂ + N ₂ P + MgN ₆
12.22	41.5	19.1	0.02	5.70	54	N ₃ P ₂ + N ₂ P + MgN ₆ + NP
11.58	41.7	14.4	0.05	5.41	65	N ₃ P ₂ + MgN ₆ + NP
10.34	37.9	17.8	0.14	5.40	53	MgN ₆ + MgN ₂
10.72	39.8	14.6	0.16	5.30	63	MgN ₆ + MgN ₂ + NP
10.88	40.4	14.9	0.12	5.20	63	MgN ₆ + MgN ₂
11.25	41.9	11.5	0.09	5.17	73	N ₃ P ₂ + MgN ₆ + NP
11.15	42.1	11.1	0.15	5.10	74	N ₃ P ₂ + MgN ₆ + NP + MgN ₂
11.04	42.6	10.4	0.15	5.00	76	N ₃ P ₂ + MgN ₂ + NP + N ₂ P ₂
10.72	42.0	10.3	0.14	4.89	76	N ₂ P ₂ + NP + MgN ₂
9.32	38.8	10.1	0.11	4.50	74	N ₂ P ₂ + NP + MgN ₂
8.62	36.8	10.5		4.30	71	N ₂ P ₂ + NP + MgN ₂

^a MgN₆ = Mg(NH₄)₆(P₂O₇)₂·6H₂O, MgN₂ = Mg(NH₄)₂P₂O₇·4H₂O, N₄P₂ = (NH₄)₄P₂O₇, N₂P = (NH₄)₂HPO₄, N₃P₂ = (NH₄)₃HP₂O₇·H₂O, NP = NH₄H₂PO₄, and N₂P₂ = (NH₄)₂H₂P₂O₇.

Figure 1. The system MgO-NH₃-H₃PO₄-H₄P₂O₇-H₂O at 25 °C.

results are shown in Table I. Since the maximum MgO content is 0.16%, the solubility diagram in Figure 1 is essentially a projection on the section NH₃-H₃PO₄-H₄P₂O₇-H₂O (Frazier et al., 1973). The validity of this representation is shown by a comparison of the nitrogen and phosphate concentrations (Table I), where essentially no change resulted from the addition of magnesium to the four-component system. The first point in Table I was included to test the possibility of a soluble magnesium-amine complex, and this type of compound usually forms at unusually high ammonia concentrations. Apparently no increase in MgO is obtained by such a reaction.

RESULTS AND CONCLUSIONS

Figure 1 shows that in ammonium polyphosphate solutions, the magnesium concentration is controlled by either Mg(NH₄)₆(P₂O₇)₂·6H₂O or Mg(NH₄)₂P₂O₇·4H₂O. The monoclinic dimorph of Mg(NH₄)₂P₂O₇·4H₂O was the prevalent form in these pure systems studied, whereas the orthorhombic dimorph is the form that is found in fertilizers prepared from wet-process phosphoric acid. An

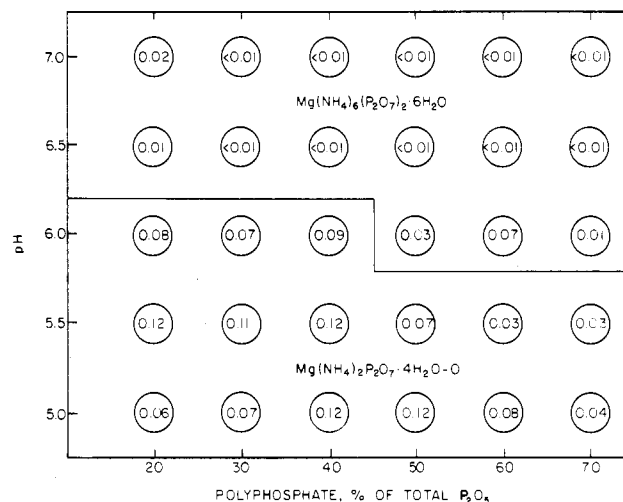


Figure 2. MgO saturation levels vs. polyphosphate content and pH in liquid fertilizers.

attempt was made to find the field boundary between the dimorphic forms, but the necessary equilibration periods were prohibitively long since both salts have very slow rates of solution. Table I shows the maximum magnesium oxide content to be 0.16% at pH 5.30; however, above pH 6, which is the desired range for fluid fertilizers, the saturation level drops to 0.01%. The precipitation of struvite, MgNH₄PO₄·6H₂O, is not a factor in polyphosphate fluid fertilizers since it occurs below 20% pyrophosphate, which is below the level normally employed to sequester iron and aluminum.

These low saturation values are in contrast to the usually observed range of 0.1–0.2% MgO for liquid fertilizers which are not saturated solutions at room temperature. Thus, the solubility of magnesium at lower ionic strengths may be different from the solubility in saturated solutions. So that data more closely related to conditions in liquid fertilizers could be obtained, ammonium polyphosphate solutions were prepared with grades (% N, % P₂O₅, % K₂O) approximating the range of 10–34–0 to 11–37–0, at 25 °C with different pH values and different proportions of ortho- and pyrophosphates and then saturated with MgO. After the solutions were equilibrated for 3 weeks

Table II. Equilibrated Solutions from the System $\text{MgO-NH}_3\text{-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$ at 25 °C

solution	composition, wt %				distribution of P, %, as			pH	solid phases ^a
	MgO	N	P ₂ O ₅	F	ortho	pyro	tri		
A-1	0.01	12.4	39.2	0.03	36	64		6.31	W
A-2	0.29	12.4	37.9	1.5				6.25	W
A-3	1.20	12.4	37.1	2.7				6.25	W
A-4	0.01	12.4	40.7	0.02	34	53	13	6.27	W
B-1	0.02	12.1	41.4	0.03	46	54		5.73	Y
B-2	0.48	12.2	39.9	1.2				5.68	Y
B-3	1.2	12.4	39.9	2.3				5.71	Y
B-4	0.03	12.4	42.1	0.04	42	45	13	5.68	Y

^a W = $(\text{NH}_4)_4\text{P}_2\text{O}_7$, $(\text{NH}_4)_3\text{HP}_2\text{O}_7\cdot\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, and $\text{Mg}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2\cdot 6\text{H}_2\text{O}$; Y = $(\text{NH}_4)_3\text{HP}_2\text{O}_7\cdot\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{Mg}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2\cdot 6\text{H}_2\text{O}$.

at 25 ± 0.1 °C, the final MgO concentrations and corresponding solid phases were determined and are shown in Figure 2.

Three points are significant: (1) the orthorhombic dimorph of $\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7\cdot 4\text{H}_2\text{O}$ is the controlling solid phase limiting the MgO content in the pH and polyphosphate regions of typical liquid fertilizers; (2) the MgO concentration pattern, which decreases almost to zero above pH 6, is of the same order of magnitude as that found for saturated ammonium phosphate solutions in the phase system studied (Table I); (3) the MgO content decreases with increasing pyrophosphate content.

Thus, the saturated and unsaturated liquids at all pyrophosphate levels and pH values above 5.7 have a MgO equilibrium saturation value below 0.1%. There is a small increase at pH 6.0 when the pyrophosphate is below 50% (0.08% MgO as compared to 0.02% for the saturated system).

Since these values are lower than those found in commercial ammonium polyphosphate liquid fertilizers (up to 0.2% MgO), the magnesium concentration is not controlled exclusively by simple solubility relationships involving the constituent species Mg^{2+} , NH_4^+ , and ortho- and pyrophosphate and their equilibrium solid phases. Furthermore, the decrease in MgO content with increasing levels of pyrophosphate precludes any significant formation of soluble complexes between magnesium and pyrophosphate.

The effect of foreign ions on magnesium solubility was investigated in an experiment designed to test the effect of tripolyphosphate ($\text{P}_3\text{O}_{10}^{5-}$) and fluoride as complexing agents for MgO since both may occur in commercial liquids. For this test the invariant solutions at pH 6.30 and 5.70 (Table I) were aliquoted into four samples, each having an excess of all four solid phases.

Sample 1 from each solution was not treated, sample 2 was charged with 1.5% F, sample 3 was charged with 2.5% F, and sample 4 was charged with $(\text{NH}_4)_4\text{HP}_3\text{O}_{10}$ equivalent to 15% tripolyphosphate expressed as percent of the total P_2O_5 . The fluorine content was obtained by using NH_4HF_2 (66% F) which had no effect on the pH and only a slight effect on ammonia concentration. The samples were equilibrated at 25 °C for 6 weeks before the super-

natant liquor was sampled for chemical analysis. Microscopic analysis of the solid fraction confirmed that the four solid phases were still present. The results are shown in Table II.

The addition of tripolyphosphate in an amount corresponding to 13% of the total P_2O_5 (40–42%) had no significant effect on increasing the concentration of dissolved magnesium. The addition of fluorine demonstrated again (Frazier et al., 1972) the formation of soluble fluoride complexes that increased the concentration of dissolved magnesium. For example, at pH 5.7 the addition of 1.2% fluorine increased the MgO concentration from 0.02 to 0.048%. At a pH of 6.3, the addition of 1.5% fluorine increased the MgO concentration from 0.01 to 0.29%, and a further increase in fluorine (2.7% F) markedly increased the concentration of dissolved MgO to 1.20%.

Thus, the magnesium in excess of that required to satisfy the solubility product relationships as Mg^{2+} ion must occur in complexed form—apparently as fluoride complexes rather than as a tripolyphosphate complex ion. With the exception of solution A-2 (Table II), the mole ratio of added fluorine to MgO solubilized indicates an $[\text{MgF}_x]$ complex, where x is in the range of 4–5. The presence of adequate fluorine in ammonium polyphosphate liquid formulations can effectively increase the “saturation” limit for the MgO impurity above the level that is likely to occur with impure commercial wet-process phosphoric acids. If the long-range outlook is a further decline in the quality of phosphate rock, including the possible utilization of marginal phosphates—especially those containing dolomite—then the sequestration principle for controlling magnesium based on fluorine complexing will become increasingly important (Frazier et al., 1972).

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