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Magnesium Ammonium Phosphates, Related Salts and Their Behavior in Compound Fertilizers

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Fluorine forms a previously unknown compound $MgNH_4HFPO_4$ (MAFP) when monoammonium phosphate made from wet-process phosphoric acid is treated with magnesium hydroxide above about 75°C in the presence of moisture. When treatment is conducted with a large quantity of water, fluorine forms a gelatinous material which resembles MAFP in chemical composition. Wet-process phosphoric acid ammoniated and reacted with magnesium hydroxide above about 75°C gives a very thick slurry, which almost solidifies due to the formation of gelatinous material, while the acid treated in the same way after being defluorinated gives a less viscous slurry in which most of the magnesium is present in the form of $MgNH_4PO_4{\cdot}H_2O$ (MH). Fluorine shows less effect at lower temperature. When treated below about 60°C, most of the magnesium combines to form $MgNH_4PO_4{\cdot}6H_2O$ (M6H) and $Mg(NH_4)_2(HPO_4)_2{\cdot}4H_2O$ (M4H). M6H and M4H decompose during drying at about 100°C, losing ammonia and water of crystallization to form amorphous materials. The decomposition is promoted by the presence of potassium salts resulting in the formation of water-insoluble potassium. Another previously unknown compound, $MgKHFPO_4$ (MKFP), which is isomorphic with MAFP has also been identified. MKFP is less soluble in water while MAFP decomposes in water to precipitate amorphous material and M6H. Solid solutions of MAFP and MKFP are often present in commercial fertilizers, and provide a small amount of water-insoluble potassium. M4H decomposes rapidly in water to precipitate M6H. M6H and MH are less soluble in pure water but are considerably soluble in water which contains acidic salts, such as monoammonium phosphate.

Recently a large number of compound fertilizers containing magneisum with grades 12—26—10—5, 12—16—14—4, 11—11—11—4, *etc.* have been produced in Japan. The main source of magnesium is magnesium hydroxide precipitated from sea water, while serpentine and olivine are used in a few plants. It has been generally thought that most of the magnesium would combine to form $MgNH_4PO_4{\cdot}H_2O$ (NH) and $MgNH_4PO_4{\cdot}6H_2O$ (M6H) in the fertilizers, both of which are less soluble in water and have good agronomic response as slow release fertilizers.

The present quantitative X-ray analysis on commercial products, however, showed that M6H is seldom present in the final products, and that although MH is often present, the yield is usually much lower than expected. Moreover, there are the following problems: (1) The products of reaction of magnesium hydroxide with ammonium phosphate and other materials are usually so sticky or viscous that cause much trouble in granulation.

(2) A considerable amount of potassium, up to 10% of the total, is sometimes changed into a water-insoluble form.

(3) Usually 30 to 35% of magnesium in the products is soluble in water when tested by the standard Japanese method.

The reasons for the above problems were not clear. The authors studied the forms and properties of magnesium compounds in compound fertilizers, and their behavior during production processes in order to clear up these problems.

Examples of Commercial Compound Fertilizers Tested

Ten examples of commercial compound fertilizers containing magnesium are shown in Table 1.

Sample No. 1 was produced with wet-process phosphoric acid, ammonia, amonium sulfate, urea, potassium chloride and magnesium hydroxide. Samples No. 2 and 3 were produced with ammonium chloride instead of the ammonium sulfate and urea of sample No. 1. Samples No. 4 and 5 were produced with potassium sulfate instead of the potassium chloride of sample No. 1. Samples No. 6 to 8 were made with powdered monoammonium phosphate made from wet-process phosphoric acid, ammonium sulfate, urea, potassium sulfate and magnesium hydroxide. Samples No. 9 and 10 were produced with wet-process phosphoric acid, sulfuric acid, olivine, ammonia and potassium chloride. Samples No. 6 to 8 were granulated at 50 to 60°C, others at 80 to 90°C. All of the granulated products were dried at about 100°C.

The water-solubility of the magnesium present in the samples ranged from 31 to 34%. The water-solubility of potassium ranged from 95 to 98% for samples No. 1 to 5 which were granulated at 80 to 90°C, and 90 to 92% for samples No. 6 to 8 which were granulated at 50 to 60°C.

Materials Used

For preparation tests in the laboratory, five samples of commercial ammonium phosphate made from wet-process phosphoric acid, and one sample each of wet-process phosphoric acid and magnesium hydroxide made from sea water were used. The chemical compositions of these samples are given in Table 2.

X-Ray tests of the ammonium phosphate samples showed that the water-soluble P_2O_5 of samples A, B, C and D was present as monoammonium phosphate, while that of sample E was present as

TABLE 1. COMMERCIAL COMPOUND FERTILIZERS CONTAINING MAGNESIUM

No.	Grade	MgO, %			K_2O, %		
		T*	WS**	WS/T	T	WS	WS/T
1	14-18-14-6	7.4	2.3	31.1	15.2	14.8	97.4
2	12-16-14-4	4.5	1.5	33.3	15.4	14.9	96.8
3	12-16-14-4	4.5	1.1	31.1	15.6	14.9	95.5
4	12-26-10-5	5.8			10.6	10.4	98.1
5	12-26-10-5	5.0			10.8	10.5	97.3
6	12-26-10-5	6.0			12.1	10.9	90.1
7	12-26-10-5	6.0			11.4	10.4	91.2
8	12-26-10-5	6.1			11.6	10.7	92.2
9	10-14-12-4	5.0	1.7	34.0	12.9		
10	11-11-11-4	4.9	1.6	32.7	11.8		

* Total. ** Water-soluble.

TABLE 2. CHEMICAL COMPOSITION OF MATERIALS USED (%)

	Ammonium phosphate					Wet-process phosphoric acid	Magnesium hydroxide
	A	B	C	D	E		
N	12.3	12.3	11.7	10.9	13.4		
T-P_2O_5	50.9	48.3	51.2	49.7	53.2	28.0	
S-P_2O_5*	50.9	48.2	50.4	48.9	52.9		
WS-P_2O_5	47.7	44.4	45.1	41.4	47.4		
SO_3	5.5	7.3	4.4	6.0		4.9	1.2
R_2O_3	3.2	3.6	4.1	5.5		1.5	0.3
MgO	0.8	1.2	1.2	2.0	0.9	0.4	64.2
CaO	0.2	0.2	0.2	0.7		0.2	0.3
F_2	3.0	3.7	4.2	3.0	1.5	2.2	
pH**	3.9	4.1	4.0	4.0	5.7		

* Petermann's citrate-soluble. ** In 10% aqueous solution.

both monoammonium and diammonium phosphates. Considerable amounts of ammonium sulfate and a water-insoluble compound "S",[1] which is likely to have the formula $Al_3(NH_4)_5H_2\cdot(PO_4)_4F_4$,[2] were present in all samples of ammonium phosphate.

Reagent grade monoammonium and diammonium phosphates, magnesium hydroxide, ammonium fluoride, hydrofluoric acid, ferric and aluminum phosphates, *etc.*, were also used for the tests.

Experimental and Results

Preparation of Standard Samples. Standard samples of $MgNH_4PO_4\cdot H_2O$ (MH), $MgNH_4PO_4\cdot 6H_2O$ (M6H) and $Mg(NH_4)_2(HPO_4)_2\cdot 4H_2O$[3] (M4H) were prepared in the following way with reagent grade chemicals:

MH: In 500m*l* of phosphoric acid (30% P_2O_5), 100 g of magnesium hydroxide was dissolved. Concentrated aqueous ammonia was added to the solution at 95°C until the pH reached about 8. The precipitate was filtered, quickly washed with hot water and acetone, and dried at 50°C.

M6H: Concentrated aqueous ammonia was added to the magnesium phosphate solution below 50°C. The precipitate was filtered, washed with water and acetone, and dried at 50°C.

M4H: A mole of finely ground monoammonium phosphate and a half mole of magnesium hydroxide were mixed and allowed to react at about 50°C by the repeated addition of small amounts of water and mixing. The product was dried at 50°C.

Chemical and X-ray analyses of the products showed they were sufficiently pure for standard samples. All of the products consisted of small crystals of less than 5 microns, similar to those present in commercial and granulator products of compound fertilizers containing magnesium.

Quantitative X-Ray Analysis. The amounts of MH, M6H and M4H present in the commercial and laboratory products were determined by quantitative X-ray analysis using spinel as an internal standard.[4,5] Calibration curves for the determinations were obtained through tests with synthetic samples. The diffraction angle and height ratio of the peaks of each compound to that of spinel at a 2θ of 36.8° by Cu$K\alpha$ ray when each compound and spinel are present in equal amounts are shown in Table 3.

TABLE 3. DIFFRACTION ANGLE (2θ, Cu$K\alpha$) AND HEIGHT RATIO

Compound	2θ	Ratio
MH	31.8	0.78
MH	10.0	0.50*
M6H	15.7	0.33*
M6H	21.3	0.28
M6H	33.2	0.28
M4H	17.0	0.38

* Less reliable because the height varies considerably with crystal size and shape.

Magnesium Compounds in Commercial Products. A quantitative X-ray analysis of magneisum compounds was conducted on eight samples of commercial products.

Most of samples contained MH, while M6H and M4H were not detected in any of the samples. The amounts of MH present and the yields (MgO present as MH per cent of total MgO) are shown in Table 4.

TABLE 4. THE AMOUNT AND YIELD OF MH

Sample No.	1	2	3	6	7	8	9	10
MH, %	15	4	3	0	1	1	4	10
Yield, %	53	23	17	0	4	4	21	53

The yields were less than about 50%, and was especially low for samples No. 6 to 8, which were granulated at 50 to 60°C and dried at about 100°C. Unreacted magnesium hydroxide was detected only in small amounts in samples No. 1 to 3. Considerable amounts of an unknown compound were detected in samples No. 1 to 3. Other magnesium compounds were not detected.

These results indicate that a considerable portion of magnesium may be present as the unknown compound in samples No. 1 to 3, and as amorphous material in other samples.

Reaction Products of Reagent Grade Monoammonium Phosphate and Magnesium Hydroxide. Finely powdered reagent grade monoammonium phosphate and magnesium hydroxide were blended together in various ratios, and allowed to react at temperatures between 40 and 100°C for 30 min in water vapor. The products were checked by quantitative X-ray analysis. The relations among temperature, mole ratio P_2O_5/MgO and compound formed is shown in Fig. 1.

MH formed above 75°C, M6H below 65°C and the mixture between 65 and 75°C as were previously reported.[6] In addition, M4H formed below 65°C when the mole ratio was greater than 0.5. M4H did not form but M6H did in the presence of a large quantity of water, even when

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[1] J. Ando and T. Akiyama, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1056 (1965).

[2] J. Ando, A. W. Frazier and J. R. Lehr (paper under preparation).

[3] Crystallographic Properties of Fertilizer Compounds, *Chem. Eng. Bull.* No. 6, TVA, May 1967.

[4] J. Ando and T. Akiyama, *Japan Analyst*, **13**, 717 (1964).

[5] J. Ando, J. P. Smith, M. R. Siegel and J. E. Jordan, *J. Agr. Food. Chem.*, Vol. 13, No. 2, 186 (1965).

[6] S. Iwata, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **62**, 1668 (1959).

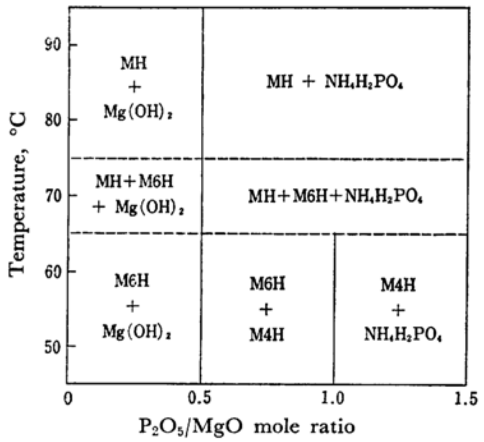

Fig. 1. Compounds present in the reaction products of reagent grade monoammonium phosphate and magnesium hydroxide.

($MH=MgNH_4PO_4\cdot H_2O$, $M6H=MgNH_4PO_4\cdot 6H_2O$, $M4H=Mg(NH_4)_2(HPO_4)_2\cdot 4H_2O$)

the mole ratio was greater than 0.5 and treatment was carried out below 65°C. In all of the tests, magnesium hydroxide reacted rapidly and quantitatively.

Reaction of Magnesium Hydroxide with Ammonium Phosphate made from Wet-process Phosphoric Acid. Similar tests were conducted with reagent grade magnesium hydroxide and the five samples of commercial ammonium phosphate made from wet-process phosphoric acid.

When the four samples of monoammonium phosphate A, B, C and D were treated above about 75°C in water vapor, only a part of the magnesium formed MH, and the yield of MH decreased linearly as the mole ratio P_2O_5/MgO increased (Fig. 2). During treatment, magnesium hydroxide reacted completely and an unknown compound, similar to that detected in commercial compound fertilizers No. 1 to 3, formed.

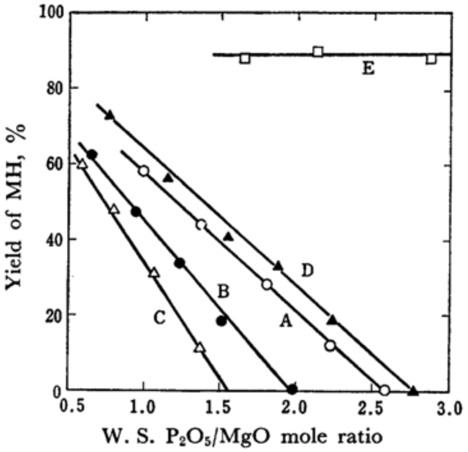

Fig. 2. Relation between the yield of $MgNH_4PO_4\cdot H_2O$ and the mole ratio of water-soluble P_2O_5 of ammonium phosphate to MgO of magnesium hydroxide.

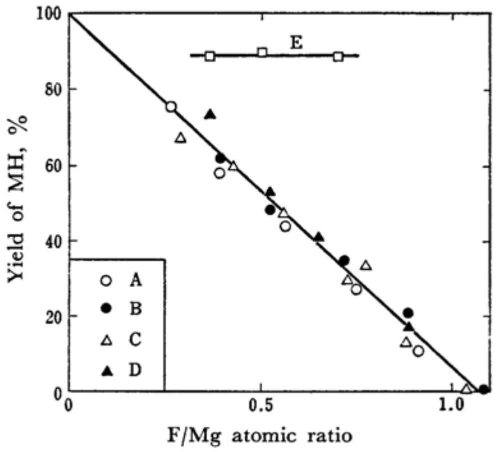

Fig. 3. Relation between the yield of $MgNH_4PO_4\cdot H_2O$ and the F/Mg atomic ratio.

Through further tests it was found that fluorine in the samples of monoammonium phosphate was the cause of the formation of the unknown compound and the decrease in yield of MH. Figure 3 shows that for samples A, B, C and D, the yield decreases linearly on the same line as the atomic ratio F/Mg increases. Figure 3 also indicates that the unknown compound contains fluorine and magnesium in the atomic ratio of 1.

When sample E, which contained diammonium phosphate besides monoammonium phosphate, was used, magnesium hydroxide reacted very slowly releasing much ammonia; nearly 90% of the magnesium combined to form MH, regardless of the P_2O_5/MgO and F/Mg ratios (Figs. 2 and 3). The unknown compound formed in small amounts.

When samples A, B, C and D were allowed to react with magnesium hydroxide above about 75° in the presence of a large quantity of water or in a slurry state, the yield of MH decreased with increase in F/Mg ratio in the same manner as in the above tests, but the unknown compound was not detected in the products. An amorphous material formed instead of the unknown compound.

Fluorine showed less effect at lower temperature. Most of the magnesium combined to form M6H and M4H when the samples of ammonium phosphate were treated with magnesium hydroxide below about 60°C.

Tests were also conducted with magnesium hydroxide which was made from sea water and ground to minus 30 mesh. The results were similar to those obtained with reagent grade hydroxide, except that the hydroxide obtained from sea water reacted slowly because of the larger grain size.

Synthesis and Characterization of the Unknown Compound. The unknown compound was prepared in several ways using reagent grade chemicals. The best sample was obtained by the following method:

One tenth mole of magnesium hydroxide was mixed with equimolecular ammonium fluoride. An amorphous material formed, losing ammonia. Two tenths mole of monoammonium phosphate was mixed with the above product and the result heated at 90 to 100°C for one hour in water vapor. The product was washed with 2% aqueous ammonium fluoride solution on a fritted glass filter with suction, and then washed with acetone and dried at room temperature. The chemical composition of the product is shown in Table 5.

Table 5. Chemical composition of the synthetic sample

	MgO	$(NH_4)_2O$	HF	P_2O_5
Composition (%)	22.49	16.50	11.58	41.83
Mole ratio	1.00	0.56	0.99	0.53

From chemical analysis, this compound was identified as $MgNH_4HFPO_4$, which should be called magnesium ammonium hydrogen filuroide phosphate and will be abbreviated to MAFP. Synthetic MAFP consisted of very small crystals of less than 0.1 μ in size. X-Ray diffraction data are shown in Table 6.

Table 5 shows that $(NH_4)_2O$ and P_2O_5 are present in slight excess. It is likely that a small amount of ammonium phosphate is absorbed by the fine crystals of MAFP. Excessive ammonium phosphate was used for preparation to promote the formation of MAFP. It was difficult to remove all of the remaining ammonium phosphate because the fine crystals of MAFP tend to decompose in washing.

Chemical analysis also shows that a considerable amount of water (about 8%) is contained in the product. By heating the product at 100°C in air, nearly all the water was removed, which resulted in considerable shrinkage of the crystal lattice as shown in Table 6. Shrinkage with heating hardly occurred when ammonium phosphate coexisted.

When the preparation of MAFP was conducted in a slurry by adding a large amount of water, an amorphous material or a mixture of MAFP with amorphous material was obtained. The amorphous material contained nearly equimolecular MgO and HF, similar to MAFP, but contained less $(NH_4)_2O$ and P_2O_5 than was contained in MAFP.

An amorphous material instead of MAFP formed also when preparation was conducted below about 60°C either with much or little water.

When preparation of MAFP was conducted at 90 to 100°C in the presence of a small amount of water using a mixture of monoammonium and diammonium phosphates, magnesium hydroxide reacted very slowly releasing ammonia; the product contained MH and less MAFP in the same manner as in the test with commercial ammonium phopshate E, indicating that only a part of the fluorine forms MAFP at high pH.

Another previously unknown compound, $MgKHFPO_4$ (MKFP), magnesium potassium hydrogen fluoride phosphate, was prepared in a similar way, treating one tenth mole each of potassium fluoride and magnesium hydroxide with one tenth mole of monopotassium phosphate at 90 to 100°C in water vapor, and washing with 2% aqueous potassium fluoride solution and acetone.

X-Ray diffraction data on MKFP are shown in Table 6. The synthetic MKFP also contained 5% water. Heating at 100°C removed the water and a slight shrinkage of the crystal lattice occurred. The synthetic MKFP consisted of small crystals less than 0.1 micron in size.

MKFP is isomorphic with MAFP and they form a continuous solid solution in each other. The unknown compound detected in the commercial products No. 1 to 3 was identified as a solid solution of MAFP and MKFP. The solid solution also consisted of small crystals less than 0.1 μ in size. X-Ray diffraction data on the solid solution obtained from sample No. 2 by removing water-soluble salts rapidly with small amount of water are also shown in Table 6. Considerable shrinkage of the crystal lattice was also observed to occur upon heating the solid solution at 100°C.

Table 6. X-Ray diffraction data on MAFP, MKFP and the solid solution

$MgNH_4HFPO_4$				$MgKHFPO_4$		Solid solution	
Synthetic		Heated at 100°C		Synthetic		Commercial product	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
13.2	100	13.0	60	13.0	40	13.1	55
7.49	12	7.37	20			7.30	10
5.82	60	5.71	60	5.68	10	5.75	50
4.33	34	4.25	40	4.19	17	4.29	40
3.93	12	3.86	10				
3.45	10	3.42	20	3.35	14	3.40	12
3.23	32	3.17	50	3.14	30	3.18	12
3.07	80	3.00	100	2.96	100	3.01	100

Viscosity of the Slurry formed by Reaction of Magnesium Hydroxide with Ammonium Phosphate. The wet-process phosphoric acid (Table 2) was ammoniated with geseous ammonia to a pH of 4 to 5. Magnesium hydroxide obtained from sea water ground to minus 30 mesh was added to the amount to give equimolecular MgO to P_2O_5 and stirred at about 90°C. The viscosity of the slurry increased remarkably as the hydroxide reacted, and the slurry almost solidified in about 30 min. During the reaction, only a small portion of magnesium formed MH and a larger portion formed a gelationous material which resembled MAFP in chemical composition, as was already mentioned.

A similar test was conducted with wet-process phosphoric acid from which about 90% of the fluorine had been removed by adding the correct amount of potassium chloride to form potassium fluorosilicate and removing the precipitate. In this test, nearly all of the magnesium formed MH, and the slurry was fluid with a viscosity of about 1 poise.

When potassium chloride was added to the acid and the mixture used without the separation of fluorosilicate, the fluorosilicate decomposed during ammoniation and fluorine reacted to depress the formation of MH and to increase the viscosity.

Tests with reagent grade phosphoric acid, hydrogen fluoride, potassium fluorosilicate, ammonia and magnesium hydroxide also showed the remarkable effect of fluorine on the viscosity.

In another series of tests, magnesium hydroxide was first added to wet-process phosphoric acid and then ammoniated to a pH of 4 to 6. In these tests, the slurry became quite viscous and almost solidified even when the acid had been defluorinated.

Water-Slolubility of Magnesium Compounds. A test with synthetic MAFP (Table 5) showed that 25% of Mg, 55% of N and 58% of P_2O_5 were water-soluble by the standard Japanese method, in which 5 g of sample is shaken for 30 min in 400 m*l* water, made up to 500 m*l* and then filtered. X-Ray analysis showed that essentially all MAFP decomposed during the standard treatment to precipitate an amorphous material and M6H. MKFP was less soluble; about 30% decomposed and 13% of magnesium was soluble in the standard method.

X-Ray tests were also conducted on commercial products No. 1 and 3 (Table 1) which contain a solid solution of MAFP and MKFP. It was found that about 90% and 60%, respectively, of the solid solution decomposed during the standard treatment. MAFP, MKFP and the solid solution are entirely soluble in 2% citric acid.

M4H decomposed rapidly in water to precipitate M6H; 18% of the magnesium was soluble in the standard method.

MH and M6H are less soluble; only 2% of magnesium dissolved in the standard method. In 100 m*l* water, 5.9 mg of MgO of MH and 4.0 mg of MgO of M6H dissolved.

Tests were made on the effect of the coexistence of several salts on the solubility of magnesium of MH and M6H. The synthetic sample (1 g each) was shaken for 30 min in 100 m*l* of 0.1, 0.5 and 2.5% aqueous solutions of monoammonium phosphate, ammonium sulfate, ammonium chloride, potassium chloride, diammonium phosphate and urea. The amounts of MgO (mg) which dissolved in 100 m*l* of the solutions of monoammonium phosphate, ammonium sulfate and ammonium chloride are shown in Table 7.

TABLE 7. MgO DISSOLVED IN 100 m*l* OF THE SOLUTIONS (mg)

Salt	Form of magnesium compound	Concentration 0.1	0.5	2.5
$NH_4H_2PO_4$	MH	24.9	35.3	58.9
	M6H	11.5	—	40.1
$(NH_4)_2SO_4$	MH	12.6	14.7	16.5
	M6H	3.9	4.2	8.3
NH_4Cl	MH	12.1	13.1	15.4
	M6H	4.0	4.2	7.1

Table 7 shows that the water-solubility is increased remarkably by $NH_4H_2PO_4$, and significantly by $(NH_4)_2SO_4$ and NH_4Cl. Tests with the other compounds showed that potassium chloride and urea have little effect, and that diammonium phosphate reduced the solubility slightly. The solubility depends mainly upon the pH of the solutions.

Tests were also made on the solubility when a mixture of salts was present. When 15 parts of MH was blended with 15 parts of NH_4Cl, 20 parts of KCl, 40 parts of $(NH_4)_2SO_4$ and 10 parts of $NH_4H_2PO_4$ to give a 15-13-12-4 grade fertilizer and tested by the standard method, 44.3% of the magnesium present dissolved. When M6H, instead of MH, was used, 34.0% dissolved.

These results show that water-soluble magnesium in commercial fertilizers can be derived from the above magnesium compounds.

Thermal Changes. Thermal gravimetric analysis curves of the synthetic samples of MH, M4H, M6H and MAFP obtained during heating at a rate of 2°C/min are shown in Fig. 4.

Iwata⁶⁾ reported that M6H (crystals 20 to 120 μ in size) converted to MH at about 150°C. The

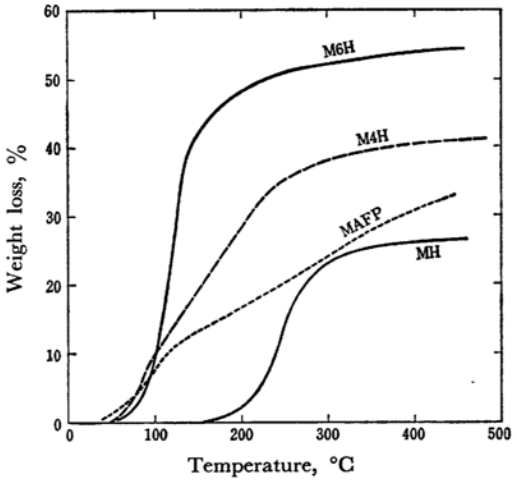

Fig. 4. Weight loss (%) during heating at a rate of 2°C/min.

present test showed that M6H began to decompose at about 60°C, losing water of crystallization and ammonia, and changed into an amorphous material at about 100°C; essentially no MH formed during heating to and above 150°C. Presumably the small crystal size (under 5 μ) is the reason for the instability.

M4H also started to decompose at about 60°C, losing water of crystallization and ammonia to form an amorphous material at about 100°C. M6H and M4H are sometimes present in the pre-mixer products and the granulator products of compound fertilizers containing magnesium. M6H and M4H in the products also consist of small crystals of less than 5 μ in size and undergo similar thermal decomposition (to be mentioned later). MH did not show any change below 150°C, and started to decompose above 160°C.

The synthetic MAFP lost about 8% water upon heating to 100°C, resulting in a considerable shrinkage of the crystal lattice, as previously mentioned. Above 100°C, MAFP started to lose ammonia, and slowly changed into an amorphous material.

A test on synthetic MKFP showed that no decomposition occurred with heating up to 150°C.

Formation of Water-insoluble Potassium. The water solubility of potassium present in compound fertilizers is apt to decrease when magnesium is present. The present tests have shown that one of the reasons for the decrease is the presence of a solid solution of MAFP and MKFP. The commercial fertilizers No. 1 to 3 (Table 1), the solubility of which ranges from 95 to 98%, contain the solid solution which partly remains undissolved in the standard treatment, as mentioned previously.

The potassium of samples No. 6 to 8 is less soluble (90 to 92%). Tests have shown that the decrease in water-solubility occurred during the drying of the granulated product at about 100°C. When magnesium hydroxide was mixed with monoammonium phosphate, ammonium and potassium sulfates and urea at 50 to 60°C for granulation, magnesium formed mainly M6H and M4H, and more than 98% of potassium was water-soluble. Both M6H and M4H decomposed into amorphous materials and the water-solubility of potassium decreased during the drying. Most of the fluorine present was in the form of potassium fluorosilicate before and after drying. The fluorosilicate was almost completely soluble in water in the standard method.

Laboratory tests have been conducted to study the relation between the decomposition of M6H and M4H and the decrease in solubility of potassium. Potassium chloride or sulfate ground to pass through a 150 mesh screen was mixed with synthetic M6H in a mole ratio MgO/K_2O of 1 : 1 and heated at temperatures between 80 and 120°C from 30 min to 7 hr. A remarkable decrease in the solubility of potassium occurred as shown in Fig. 5.

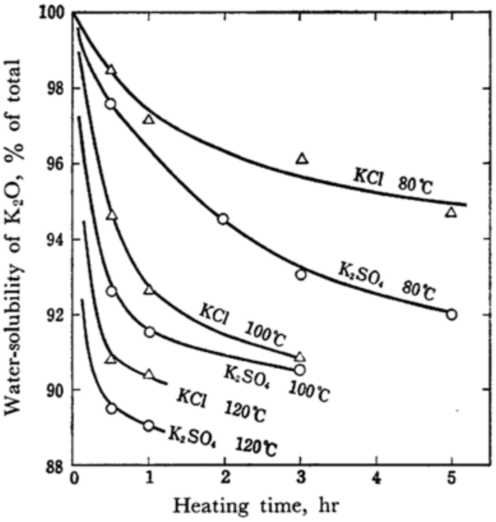

Fig. 5. Decrease of water-solubility of potassium during heating and $MgNH_4PO_4 \cdot 6H_2O$ (mole ratio $MgO/K_2O=1$).

Potassium salts were found to promote the thermal decomposition of M6H. For example, the loss of ammonia with heating at 100°C for an hour was 35% without potassium salts, 58% when potassium chloride was present, and 64% when potassium sulfate was present. Apparently, potassium combined with the amorphous material which formed by the decomposition of M6H and became insoluble in water.

An other series of tests with potassium sulfate showed that the per cent of insoluble K_2O of the total K_2O was nearly proportional to the mole ratio MgO/K_2O (Fig. 6).

Potassium nitrate gave a similar result as potassium chloride, while monopotassium phosphate showed a smaller decrease in water-solubility.

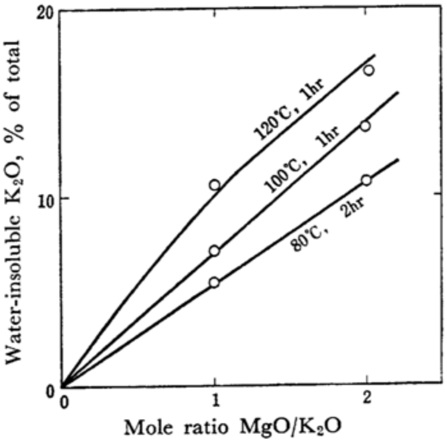

Fig. 6. Relation between mole ratio MgO/K_2O and insoluble K_2O formed by the reaction of $MgNH_4PO_4 \cdot 6H_2O$ and K_2SO_4.

For example, when mixtures of M6H and potassium salts ($MgO/K_2O=1$) were heated for an hour at 120°C, the water-solubility was 90.8% when potassium nitrate was used and 94.0% when monopotassium phosphate was used.

M4H also decomposed and combined with potassium salts during heating. The amount of insoluble potassium was roughly half that formed with M6H. For example, when a mixture of M4H and potassium sulfate ($MgO/K_2O=1$) was heated for an hour at 100°C, the water insoluble potassium was 4.1% while it was 8.6% with M6H.

MH was stable up to 150°C and did not react appreciably with potassium salts up to 130°C.

The potassium which combined with the amorphous material and became insoluble in the standard method was found to dissolve very slowly in water. For example, the water solubility of a smaple which was 89.7% by the official method increased to 92.5% when the sample was dipped in water for 5 days, and to 96.2% after 13 days.

Discussion

The present tests show that fluorine has remarkable effects on compound fertilizers containing magnesium when treated at relatively high temperatures. The weight ratio F/P_2O_5 of both wet-process phosphoric acid and ammonium phosphate made from the acid ranges from 0.05 to 0.1, and most of fluorine is usually present in fairly reactive forms. Consequently, by reaction above about 75°C, fluorine combines with 30 to 60% of the magnesium in fertilizers which have a P_2O_5/MgO weight ratio of about 3 (14–18–14–6, *etc.*), and with 50 to 100% of the magnesium in fertilizers which have a ratio about 5 (12–26–10–5, *etc.*). Fluorine thus forms MAFP, MKFP, the solid solution and a similar amorphous material, and depresses the formation of MH.

The high viscosity of the reaction products may be due to the above fluoride compounds, which consist of very small crystals under 0.1 μ in size, or a gel.

In order to eliminate the high viscosity which causes difficulties in plant operation, and to obtain products which contain most of their magnesium in the form of MH, a large portion of the fluorine should be removed or converted into a less reactive form.

Potassium fluorosilicate readily reacts with magnesium hydroxide and ammonium phosphate above about 75°C. There are indications that ammonium and sodium fluorosilicates are also fairly reactive. Those fluorosilicates should be removed from the system to eliminate the effects of fluorine. If fluorine can be converted into a less reactive form such as K_2NaAlF_6, the removal might not be necessary.

Another way to form a lot of MH in the presence of fluorine is to carry out treatment at high pH where a lot of ammonia is released. This treatment might not be favorable for plant operation because equipment for the recovery of ammonia would be necessary, the reaction of magnesium hydroxide would occur very slowly at the high pH, and moreover, the reaction products would still be fairly viscous.

The conversion of most of the magnesium into M6H and M4H when commercial monoammonium phosphate was treated with magnesium hydroxide below about 60°C is due to the poor reactivity of the fluoride compounds in the phosphate (such as $Al_3(NH_4)_5H_2(PO_4)_4$[2]) at low temperature; a test showed that fluorine, in the form of ammonium fluoride, depressed the formation of M6H and M4H below even 60°C.

M6H and M4H which forms in the pre-mixer and granulator at commercial scale plants usually consist of very small crystals less than 5μ in size and readily decompose during drying at about 100°C to form amorphous materials resulting in a remarkable decrease in the water-solubility of potassium. To prevent the great decrease in water-solubility, the drying temperature should be kept low, or magnesium hydroxide should be reacted above 75°C to prevent the formation of M6H and M4H.

By reaction at higher temperature, a solid solution of MAFP and MKFP is apt to form, giving a small amount of water-insoluble potassium. If the wet-process phosphoric acid was defluorinated or treated to convert fluorine into a less reactive form and reacted with ammonia and magnesium and potassium salts above 75°C, essentially all of the magnesium would form MH which is stable during drying, and essentially all of the potassium would be soluble in water.

Fluorine thus causes great trouble in the production of compound fertilizers containing magnesium. However, exploratory agronomic tests on barley have indicated that MAFP and the solid solution have good fertilizer value which might even be superior to MH. Further agronomic tests are in progress.