

Table VI. Apparent Diffusion Constant Estimated for Assumed Values for Extraction Depth

Moisture Content of Seed, %	W (Data from Table V)	Estimate of $D/(R + 1)$ Sq. Cm./Sec. by Eq. 5			
		$h = 0.0005$ cm.	$h = 0.0010$ cm.	$h = 0.0020$ cm.	$h = 0.0050$ cm.
18	1.6×10^{-3}	4×10^{-10}	1.6×10^{-9}	6.4×10^{-9}	4×10^{-8}
12	3.2×10^{-6}	8×10^{-13}	3.2×10^{-12}	1.3×10^{-11}	8×10^{-11}

hydroxide in aqueous medium with $D = 5 \times 10^{-5}$ sq. cm. per second [estimated according to the procedure by Wilke and Chang (5)]. It is, however, tentatively assumed that diffusion at high moisture content is taking place mainly in free and adsorbed water present in the fruit coat governed by the same diffusion constant as in a dilute aqueous solution, $D = 5 \times 10^{-5}$ sq. cm. per second. If this is correct, R comes out as $R \sim 10^3$ for $h = 5\mu$ and $R \sim 10^5$ for $h \sim 50\mu$. [Similar distribution patterns are reported for the partition of mercurial between water and cellulose fiber in the preservation of ground wood pulp and in slime control in paper mills (4).] The total average concentration of mercurial is usually of the order of 300 p.p.m. of mercury. According to Equation 1 the concentration of free mercurial C would be 0.3 p.p.m. of mercury for $h = 5\mu$ and 0.003 p.p.m. for $h = 50\mu$. According to the present hypothesis the free mercurial is dissolved in the water, which

brings these figures up to 2 and 0.02 p.p.m. of mercury, respectively, of free mercurial present in the aqueous phase. This tentative estimate may be compared with the fact that the concentration required for control of most fungi in in vitro tests is in the 0.1 to 1 p.p.m. of mercury range in case of the methylmercurials studied (2, 3).

These qualitative features indicate that the used diffusion model is not only useful for efficient reduction of the experimental data but may also provide a reasonably correct physical picture of some actual conditions.

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FERTILIZER RAW MATERIALS

Magnesium Ammonium Phosphate from Olivine and Rock Phosphate

Although dolomite inclusions have provided adequate nutrient magnesium in ordinary superphosphate, often there was insufficient room for such additions to high-analysis fertilizers. For such cases, the industry resorted chiefly to sea water magnesia and hydrated dolomitic lime. The authors propose a magnesium concentrate through sulfuric and phosphoric acid acidulations of olivine and rock phosphate, in bulk, or as leachates for ammoniations to obtain successive precipitations of dicalcium phosphate and magnesium ammonium phosphate.

MAGNESIUM REQUIREMENT in plant nutrition was not recognized generally until it was revealed most conclusively in 1923 by Garner and associates (2) that paucity of the element in soils caused "sand drown" in tobacco leaves. They found also that the calcium of limestone additions repressed effectiveness of soil content of magnesium, as was evidenced also through researches at the Tennessee Station (9, 10). These findings also negated the long-standing teachings of Loew and May (4) as to magnesium-induced chlorosis and refuted their "lime-magnesia ratio" hypothesis.

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The industry had used limestone to condition superphosphate and to protect the containing bags against free acid, but had not recognized the differential solubilities and compositions of the two carbonate minerals. Hence, limestone inclusions had been delimited to guard against percentage decrease of phosphate "availability." In 1919, however, the Tennessee Station revealed that no such effect was induced by dolomite inclusions, without limitation, and between 1922 and 1954 more than 8,000,000 tons of the mineral were utilized by the industry (13).

Later, the speed and extent of dolomite-induced transitions of monocalcium phosphate to diphosphates of magnesium and calcium in superphosphate were

determined at the Tennessee Station through periodic and protracted measurements of the carbon dioxide liberated from enclosed mixtures (11), after which discrete analyses established the proportions of the engendered diphosphates and absence of reversion (8).

Inadequacy of Dolomite for Additions to High-Analysis Fertilizers

In certain areas where fertilizers are used extensively, dolomite inclusions have provided adequate and readily available magnesium in ordinary superphosphate. But, with advent of high-analysis goods (15), often dolomite additions did not provide desired percentage of magnesium in mixtures and the industry resorted to inclusions of mineral magnesium potassium sulfate, sea water-

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derived magnesium oxide (MgO), and hydrated dolomitic lime (CaO.MgO). Moreover, except for the fusion of olivine and rock phosphate, as in the TVA process (16), no fertilizer carrier of magnesium has been developed.

The present authors proposed to utilize olivine for inclusion in superphosphate and to develop an economical process for a fertilizer rich in magnesium and suitable for ammoniation to develop magnesium ammonium phosphate, the efficacious component of Peruvian guano. Importations of that highly prized bird manure began in 1830, 14 years previous to the inauguration of the commercial fertilizer industry in the United States. In the early years, the word "guano" was used to designate commercial fertilizers and now identifies certain large fertilizer corporations.

Experimental Procedure

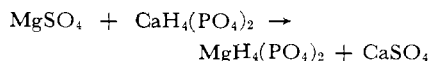
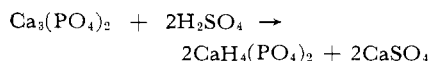
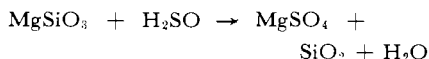
The initial experimental step was an adaptation of the "wet method," whereby rock phosphate is digested with sulfuric acid and leached to produce phosphoric acid. Olivine was used as a source of magnesium for separate additions, and for olivine-rock phosphate additions, to sulfuric acid. A primary requirement of the proposal was that the phosphate radical (PO₄) in such mixtures should be in equivalence to the potential monophosphates of the leachates. In general, the acidulations were to be without applications of heat, other than steam injections.

Acidulated mixtures of rock phosphate and sulfuric acid, 55° Bé, yielded 95% conversions of monocalcium phosphate, as was reported by Young and Heil (18). The next step was to determine whether the liberating acid, either sulfuric or phosphoric, would effect complete dissolution of olivine, added either alone or jointly with rock phosphate, and afford full recoveries of the starting contents of magnesium and calcium.

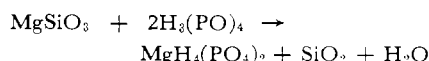
The 100-mesh olivine used was from the massive formation in western North Carolina. Its magnesium content was more than twice that of dolomite, and calcium was absent (3, 10, 11). The 100-mesh mineral phosphate was the Tennessee brown rock that carried 34% of phosphorus pentoxide.

Although incorporations of olivine and of serpentine were only meagerly soluble in soils and without benefit to vegetation (12), the two minerals reacted in mixtures with moist monocalcium phosphate, even more readily than magnesite or dolomite or their respective calcines (5).

All of the joint additions of the minerals were in relation to the magnesium and calcium contents of the charges and were potential for development of the respective monophosphates, as in the simplified equations:



and for the engendered H₃PO₄:



Results

The percentage recoveries were determined by analysis of the acidic filtrates from the respective charges of olivine.

The incomplete recoveries (80.5 and 87.6%) from sulfuric acid, 55° Bé, acidulations of 50-gram charges of raw olivine at 100° C. indicate that the liberated silica may have formed protective coatings on undissolved particles in the slurries and retarded filtration and washing.

Recoveries effected through phosphoric acid digestions of raw and calcined charges of olivine (Table I) in general, were somewhat less than the corresponding values for sulfuric acid. Raising the temperature to 90° C. and extending digestions induced somewhat larger recoveries, but the calcines yielded only slightly more to the digestions.

In obtaining a solution carrying phosphate in joint equivalence to the magnesium and calcium of a mixture of olivine and rock phosphate, it was hoped that phosphates of the two elements could be recovered separately, through pH-controlled successive ammoniations of and precipitations from the leachates. Consequently, the mixtures were added to 105% equivalence of sulfuric acid and, after 20 minutes, the digests were filtered and washed. The filtrates then were ammoniated to pH 6 to precipitate dicalcium phosphate; the magnesium content remained as monophosphate in the filtrate.

Proportions in Mixtures	
Olivine, %	Rock, %
10	90
20	80
25	75
25	75
50	50

Recoveries of magnesium at 90° C. from the corresponding phosphoric acid digests of 1 to 1 mixtures of the two minerals were complete, but the 48-hour extension of the digestions of the joint additions did not prove advantageous. The slurries of the joint charges underwent leaching more readily than those from separate charges of the minerals.

Ammoniation of Leachates

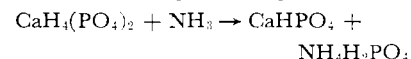
Stepwise ammoniations of the leachates permitted either fractional or com-

Table I. Magnesium Recoveries from 50-Gram Charges of Olivine Alone through Digestions with Concentrated Phosphoric Acid^a

Conditions Imposed			MgO recovery %
Prior calcination	Temp., ° C.	Digestion, hours	
None	29	24	26.1
		48	24.0
		0	38.4
500° C.	90	0	67.2
		48	70.6
		0	44.1
	90	0	60.5
		24	76.5

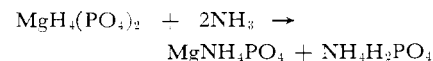
^a 79.4% H₃PO₄.

plete precipitations of dicalcium phosphate, according to the equation:



When ammoniation was restricted to 1/3 equivalence, the resultant fraction of dicalcium phosphate had a meager fluorine content, but the further precipitate was sufficiently low in fluorine to admit its use as a feed supplement.

When the filtrate from the complete dicalcium phosphate was ammoniated fully, magnesium ammonium phosphate resulted, as in the equation:



In brief, when various mixtures of olivine and rock phosphate were acidulated with equivalent sulfuric or phosphoric acid and filtered, the controlled ammoniations of the filtrates effected almost complete recoveries of the calcium and full recovery of the concomitant magnesium. The calcium phosphate was recovered in two grades, according to fluorine content. Magnesium was recovered as magnesium ammonium phosphate, the composition of its anhydride being magnesium 17.4% or MgO 29%; nitrogen 10% and phosphorus 23.2% or P₂O₅, 52.2%. In case the magnesium precipitate should be the hexahydrate, MgNH₄PO₄.6H₂O, the foregoing percentages would be lessened accordingly. The possible variables were not pursued in this exploratory work.

Conclusions

Although dolomite continues useful for the conditioning of standard superphosphate, and to supply adequate inclusions of magnesium, the concentrated superphosphates call for a material richer in magnesium and devoid of calcium. Olivine is such a material, its magnesium content being more than twice that of dolomite and, furthermore, it is more reactant with acidic phosphates.

Although it is believed that olivine, and also serpentine, could be utilized

for commercial production of magnesium ammonium phosphate, the preferred procedure would probably be ammoniation of the solid acidulates of mixtures of the two minerals. An advantageous adaptation might be their introduction with the chosen acid into the "cone mixer" developed by Bridger, Wilson, and Burt (7) and used by Yates and Williams (17) and by Young and Heil (18) for subsequent ammoniation of the resultant superphosphate. With olivine as a chosen variant for magnesium content, the resultant acidulate could be ammoniated directly—i.e., without filtration.

Although pointed to continuous acidulation of the jointly delivered minerals, the process could be adapted to batch acidulations, with or without ammoniation of leachates therefrom. One certainty and one uncertainty arise from such operations. The unfiltered acidulated mixtures become diluted by the silica (SiO₂) liberated from the olivine, but this need not become a problem where the olivine inclusions would be a small fraction of the total. The uncertainty is whether the variations in ammoniation technique would result in an anhydride or hexahydrate precipitate.

The results from the closely controlled acidulations of 50-gram charges of the mixtures of olivine and rock phosphate and ammoniations of the resultant slurries were in close accord with the values indicated by the equations, and it is believed that rigorous pilot plant trials

would demonstrate the ease and economy of the proposed procedure and production.

Important also is the fact that olivine has proved efficacious both as conditioner and for input of magnesium. Obviously, in case direct additions of the silicate to superphosphates are not to be followed by ammoniation, the mixtures should be sufficiently moist to offset the drying resultant from hydration of the two engendered diphosphates (5).

The magnesium silicate minerals occur in multiple locations in the United States. The North Carolina Conservation Commission has described and pictured the extensive and relatively accessible formations in western North Carolina and north Georgia (14), fairly close to sources of both sulfuric acid and rock phosphate, so that operation of the "wet method" upon olivine, alone and jointly with rock phosphate, and successive ammoniations of the resultant slurries might bring economic production of magnesium fertilizers of known value.

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ENZYME RESPONSE TO DIETARY SUGAR

Effect of Various Levels of Dietary Sugar on the Succinoxidase of the Liver of Swine and Cattle

THE SEARCH for new feeds is of great importance in the animal industry. Each new possibility demands tests such as rate of gain, carcass characteristics, and chemical evaluations. "Crude" sugar becomes available at times and may have special properties as an animal feed. It is partially refined sugar, fairly economical, and should be equivalent to other dietary carbohydrates. A typical analysis gives approximately the following percentages of various substances: sucrose, 88; invert sugar, 5; protein, 0.7; ash, 1.4; and water, 4.7. Wilcox *et al.* (7) fed sucrose to 95 beef cattle and 12 swine from 14 days to 6 hours before slaughter and observed that the livers of the animals fed the sucrose were larger and contained more sugars than the controls. Heck (3) found that crude sugar reduced shrinkage in swine during shipment to market, decreased shrinkage of hams during curing, and im-

proved flavor, texture, and tenderness. Shipley, Meyer, Copenhaver, and McShan (5) reported that the diabetic lactating rat has twice as much succinoxidase in the liver as normal lactating rats. They believed that such a response to excess sugar was an example of enzyme adaptation (5). Bargoni (2) found that rats fed 87% sugar diets for 25 days had approximately 20% more succinic dehydrogenase in their livers than corresponding rats that were fed casein instead of sugar. The present study was made in the light of the above reports, to determine how succinoxidase activity in the liver would be affected by sugar fed in growing-fattening diets of swine and cattle.

Procedure

Forty-seven purebred Duroc, purebred Spotted Poland China, and Spotted

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Poland China X Hampshire crossbred swine were divided into four dietary groups according to breed, sex, and weight and fed the rations shown in Table I from 9 weeks of age until they weighed 220 ± 8 pounds. All were fasted 24 hours before slaughter. As breed and sex had no effect on the data, no values are presented for these factors.

Fourteen Aberdeen Angus heifers, 15 months old, and weighing 709 ± 57 pounds each, that had been on a full feed of ground snapped corn, cottonseed meal, and alfalfa hay for 4 months, were given the dietary sugar treatments shown in Table I. The heifers were fasted 16 hours before slaughter.

Samples of liver were obtained from the swine and heifers 45 ± 5 minutes after they were sacrificed by bleeding. The samples were immediately frozen solid at -8° C. and analyzed during the following week for succinoxidase activity