Diffusion of Mercurial in the Fruit Coat of Treated Seed

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The penetration of mercurial into the fruit coat of treated seed is accompanied by a reduction of the concentration of mercurial vapor in the atmosphere surrounding the treated seed and by a decrease in the amount of mercurial that can be extracted from the outer surface layer of the seed. Extraction data may be reduced to yield a single penetration parameter using a simple diffusion model. The rate of penetration is very much influenced by the moisture content, as indicated by a 500-fold increase of the diffusion parameter when the moisture content of wheat seed was raised from 12 to 18%.

RECENT STUDIES of the mechanism of liquid seed treatment (Panogen process) have shown that the mercurials used in this process take part in diffusion and evaporation processes, which contribute to the thorough disinfection of the fruit coat of the seed (8). Further study of the diffusion process is reported here. A surface extraction method is used to ascertain the diffusion of the mercurial inward into the fruit coat. The extract is assayed for mercury by a new analytical millimicro procedure developed for these studies. An attempt is made to reduce the experimental data to a single diffusion parameter governed by the apparent diffusion constant and the standard conditions of the extraction procedure. This easily determined diffusion or penetration parameter seems to be a useful property for study of the behavior of seed treatment materials and for general studies of seed activity.

Materials and Methods

Seed-Treatment Materials and Procedure. Wheat seeds were exclusively used in the present study because of the importance of this crop. Their fairly regular shape is of advantage in connection with the surface extraction method as a reasonably uniform initial coverage is obtained in the seed treatment.

The seeds were treated in the laboratory in 100- or 500-gram batches (8). Favorable mixing conditions with the disinfectant applied initially on the walls of the bottle were used to get a uniform initial coverage. Two seed moisture contents were used: 12% and 18%, counted on the total weight of the seed. Treated seeds were stored in darkness at 20° to 21° C.

In one series, experimental Panogen formulations were used with 0.8, 1.5, and 3.0% mercury as methyl mercuric hydroxide.

In another series, seeds were treated with straight aqueous solutions and with talcum dust formulations containing 1% mercury as methyl mercuric hydroxide, cyano(methylmercuri)guanidine, ethyl

mercuric chloride, methoxyethyl mercuric acetate, and phenyl mercuric acetate. Prior to dissolution in distilled water or grinding with the dust carrier, the organomercury compounds as received from the commercial manufacturer were recrystallized twice from ethyl alcohol. Methyl mercuric hydroxide was, however, obtained from precipitated methyl mercuric iodide, which was converted to hydroxide by treatment with aqueous silver oxide. The most important check on the absence of more volatile mercury compounds was easily obtained by mercurial vapor determinations in which impurities with a higher vapor pressure—e.g., traces of metallic mercury—show up as an initial peak. The methyl and ethyl derivatives showed no peak of volatile organic mercury contaminants and exhibited no metallic mercury component. The vapor above the phenyl and methoxyethyl derivatives, however, consisted largely of metallic mercury. According to the author's experience, traces of metallic mercury can never be completely eliminated from the phenyl and alkoxyalkyl mercurials.

Mercurial Vapor Determination above Treated Seeds. The concentration of mercurials in the atmosphere surrounding the treated seed was determined by means of a mercury vapor meter with a furnace for decomposition of organic mercury compounds (8). Present equipment was, however, designed as a compact portable unit (4). Furthermore, the furnace for decomposition of organic mercurial vapor was of a different design, with the electrical heating element mounted in the furnace tube (instead of around), thus giving a direct contact between the heating element and the gas stream. The monitoring air stream was passed at a rate of 5.1 liters per minute through a bed of treated seed kept in a glass tube 55 cm. long and 3.7 cm. in diameter. Particulate matter was removed by means of a cotton filter; this was necessary because the dust formulations used in some

experiments otherwise would have given erroneously high readings due to mercurial dust removed from the seed by the air stream (6). Readings were taken 5 minutes after start of the air stream, at which time steady values were obtained. The temperature was 20° ± 1° C. in all measurements.

Surface Extraction Method. The amount of free mercurial remaining in the surface layer of the fruit coat was estimated by rapid surface extraction of the treated seed with distilled water under standard conditions. Ten grams of seed were rapidly weighed into a glass bottle; 25.0 ml. of distilled water (20° C.) were added, and the bottle was slowly shaken for 4 minutes. The water solution was then immediately decanted off into a thoroughly cleaned test tube. Any particulate matter carried over was allowed to settle; then 2.0-ml. portions of the clear supernatant water solution were taken for analysis. Because of the very high sensitivity of the chemical analysis, the samples frequently had to be diluted further before the final assay.

Mercury Analysis of Wash Solution. A new procedure for the analysis of millimicrogram quantities of mercury was used for assay of wash solutions by the surface extraction method (7).

The highly dilute aqueous solution is atomized and burned in the oxyhydrogen flame of the atomizer-burner of a Beckman flame spectrophotometer assembly. The combustion gases, containing metallic mercury vapor from the decomposed mercury compounds originally present in the sample, are passed through a series of condensers and cotton filters for removal of particulate matter and water vapor. The gas stream is finally assayed for metallic mercury vapor in the gas cell of a Kruger mercury vapor meter, Model 23. If experimental conditions are rigorously controlled, this method is capable of a very high resolution with the detection limit of 10^{-9} gram of mercury or 1 γ per liter. The coefficient of variation for duplicates amounts to 1%.

Table I. Surface Extraction and Mercurial Vapor Measurements, c_a, for Wheat Seeds (12% Moisture) as Function of Storage Time

(Temperature 20°C.)

Seed Dressing (0.2 Gram/100 Grams Seed)		t = 5 Min.		t = 1 Day		t = 1 Week		t = 1 Month	
Compound	Formulation (1% Hg)	c_a, γ Hg/cu. m.	Hg extract, %	c_a, γ Hg/cu. m.	Hg extract, %	c_a, γ Hg/cu. m.	Hg extract, %	c_a, γ Hg/cu. m.	Hg extract, %
Methyl mercuric hydroxide	Aq. soln.	180	...	70	27	39	13	12	7
	Dust	340	...	110	36	41	21	19	12
Cyano(methylmercuri)guanidine	Aq. soln.	165	...	70	37	42	24	9	8
	Dust	120	...	100	26	42	13	26	12

Theory

The earlier radioactive studies (8) and the present surface extraction studies indicate a rapid diffusion of mercurial into the fruit coat. In spite of the complexity of this process, theoretical analysis is desirable for reduction of the experimental data to a characteristic parameter. Several models of varying complexity may be set up for description of this diffusion process. The actual process takes place in an anisotropic medium and is accompanied by a number of reversible and irreversible chemical reactions which temporarily or permanently immobilize the mercurial. Diffusion models considering all these effects are very complicated. In practice it would be very difficult, if not impossible, to separate these interacting effects; therefore a simple model is chosen to get efficient reduction of experimental data.

In Figure 1 the surface layer of a seed kernel is represented as a plane slab. The seed dressing is initially applied as a very thin and uniform layer in plane A, which represents the surface of the kernel (Figure 1).

Diffusion of mercurial from this plane source toward the interior of the kernel is assumed to be governed by the diffusion constant D. Furthermore it is assumed that diffusion is retarded by a chemical reaction which immobilizes the diffusing mercurial. This reaction is assumed to be very rapid, so that local equilibrium exists between free and immobilized mercurial. It is assumed that the concentration of the immobilized mercurial, S, is proportional to the concentration of free mercurial, C.

$$S = R \times C \qquad (1)$$

Under these conditions diffusion will proceed as if governed by a diffusion constant with the value $D/(R + 1)$ (1). The concentration distribution of free mercurial is then (1) given by the relation

$$C = \frac{M}{\sqrt{t \pi D/(R + 1)}} e^{-X^2/\{4tD/(R + 1)\}} \qquad (2)$$

where M is the amount of mercurial originally deposited on the source plane (A, Figure 1), X is the distance from this plane and t symbolizes time. Some curves are shown in Figure 1 which rep-

resent concentration distributions for various values of the parameter $tD/(R + 1)$.

In the surface extraction procedure a part of the fruit coat is subjected to extraction, as indicated on Figure 1. It is assumed that a constant fraction, K, of the free mercurial in this zone is extracted under the standardized conditions of this experiment. The amount of extracted mercurial, E, is then

$$E = \int_0^h KCdx = K \int_0^h Cdx \qquad (3)$$

where h is the depth of the extraction zone and C is governed by Equation 2.

The experimental studies give E as a function of time t. Four parameters are unknown (D, R, K, and h), which cannot be separated by the present method. If these parameters are reasonably constant in a series with E as a function of t, a parameter may, however, be derived which is proportional to the apparent diffusion constant D ($R + 1$) and otherwise governed by the experimental conditions. Substitution of η^2 for $X^2/\{2tD/(R + 1)\}$ transforms Equation 3 into

$$E = \frac{2KM}{\sqrt{2\pi}} \int_0^z e^{-\eta^2/2} \times d\eta =$$
$$2 KM \int_0^z \phi(n) \, dn \qquad (4)$$

where

$$z = h \sqrt{(R + 1)/(2tD)}$$

and $\phi(\eta)$ is the normal curve of error.

The product, KM, represents the amount of mercurial extracted when no mercurial has diffused out of the extraction zone (Figure 1). KM is thus evaluated as the limit value for E when $t \to 0$. It is then evident from Equation 4 that parameter z can be obtained from statistical tables for the normal curve of error using the entry $E/(2KM)$. Since $z = h \sqrt{(R + 1)/(2tD)}$, a plot of z as a function of $\sqrt{1/t}$ should give a straight line with the slope equal to $h/\sqrt{2 D (R + 1)}$.

The extraction depth, h, is governed by the properties of the seed under study and by the extraction procedure. This parameter, h, is believed to be roughly constant for a particular kind of seed even in experiments in which the moisture content is varied, because in the
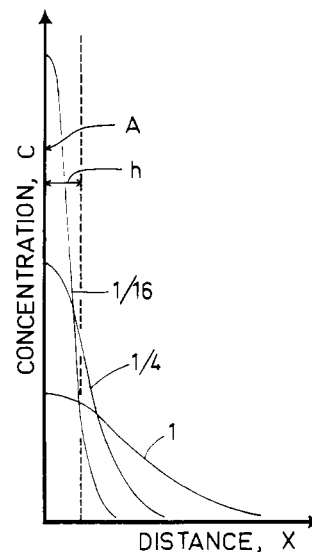
Figure 1. Schematic representation of mercurial diffusion in the fruit coat of treated seed

Numbers on concentration-distance curves are values for $tD/(R + 1)$. Mercurial initially applied in plane A, extraction depth $= h$

extraction procedure the surface layer will be soaked with water to the extent that initial differences in moisture content may be of little importance.

Reduction of extraction data in the indicated way thus produces a parameter, W, which is proportional to the apparent diffusion constant, $D/(R + 1)$.

$$W = \{D/(R + 1)\} \times (1/h)^2 = 1/\{2tz^2\} \qquad (5)$$

W gives valuable information with respect to the penetration ability of different fungicides. Furthermore, surface extraction with evaluation of W seems to constitute a useful tool in studies of the biological activity of seeds, particularly at various moisture content levels.

The concentration of mercurial, c_a, in the atmosphere surrounding treated seeds should be proportional to the activity in the physicochemical sense, of the mercurial in the surface layer of the fruit coat. Assuming ideal conditions with activities equal to concentrations, linear proportionality should be observed between c_a and E, as E is likely to be proportional to the amount of free mercurial in the surface layer of the fruit coat (the extraction zone).
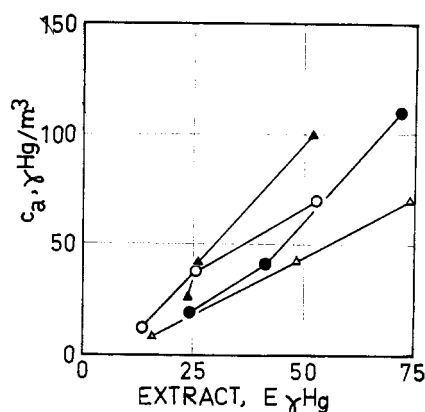
Figure 2. Mercurial in atmosphere above treated seed, c_a, plotted against amount of mercury, E, removed from surface in extraction procedure

O Methylmercuric hydroxide solution
● Dust
△ Cyano(methylmercuri)guanidine solution
▲ Dust

Experimental Results and Discussion

Comparison between Surface Extraction and Vapor Pressure Measurements. Wheat seeds with normal moisture content (12%) were treated with dust and liquid formulations containing 1% mercury as methyl mercuric hydroxide, cyano(methylmercuri)guanidine, ethyl mercuric chloride, methoxyethyl mercuric acetate, and phenyl mercuric acetate.

Determinations of mercurial in air and surface extractions were performed at various times after the treatment. Table I shows the simultaneous decrease of these two quantities with time. The liquid and dust formulations exhibit no marked differences in this experiment, except for the higher initial c_a value for the methylmercuric hydroxide dust due to the higher vapor pressure for solid methylmercuric hydroxide compared to its dilute aqueous solution [Table II, (8)].

The nonsorbent talcum carrier used in these tests should cause no vapor pressure reduction of practical importance. Under these conditions the vapor pressure of the mercurials studied is evidently high enough to permit essentially complete evaporation from the dust within less than one day. This was confirmed by analysis of washed off particulate matter, mainly the dust carrier, which contained no (or very little) mercury. Differences in vapor action between liquids and dusts are not expected.

Similar results are reported in Table II. The low value for the aqueous ethyl mercuric chloride formulation is due to the fact that this compound had to be hydrolyzed to the hydroxide because of the low aqueous solubility of the chloride. No organic mercury was detected above seeds treated with phenyl and methoxyethyl derivatives; readings are due to traces of metallic mercury.

Figure 2 shows c_a plotted as a function of extractable mercurial, E (data from

Table II. Mercurial Vapor Measurements, c_a, for Wheat Seeds (12% Moisture) Treatment with Defined Laboratory Formulations

Seed Dressing (0.2 Gram/100 Grams Seed)

Compound	Formulation (1% Hg)	c_a, γ Hg/Cu. M., at 20° C.	
		t = 5 min.	t = 1 day
Methyl mercuric hydroxide	Aq. soln.	180	70
	Dust	340	110
Cyano (methylmercuri)guanidine	Aq. soln.	165	70
	Dust	120	100
Ethyl mercuric chloride	Aq. soln.[a]	140	68
	Dust	1400	74
Methoxyethyl mercuric acetate	Aq. soln.	35[b]	14[b]
	Dust	88[b]	25[b]
Phenyl mercuric acetate	Aq. soln.	19[b]	0[b]
	Dust	5[b]	1

[a] Dissolved by addn. of NaOH and therefore present as C_2H_5HgOH.
[b] Largely metallic mercury vapor.

Table III. Surface Extraction of Wheat Seeds Treated with Experimental Panogen Formulations Containing Methyl Mercuric Hydroxide

Seed Dressing			Extract from 10 Grams of Seed, E γ Hg				
Hg concn. wt./vol., %	Dosage, ml./100 grams	Moisture Content of Seed, %	t = 5 min.	t = 15 min.	t = 35 min.	t = 2 hours	t = 1 month
0.8	0.200	12	51.2	53.8	44.6	38.0	8.4
			49.0	53.5	45.5	49.9	9.8
1.5	0.107	12	52.5	49.6	44.1	55.6	9.4
			52.5	43.7	43.1	33.6	25.8
3.0	0.053	12	86.1	92.3	98.3	71.1	11.5
			110.5	114.6	81.3	78.4	11.6
0.8	0.200	18	21.6	27.1	9.8	10.9	0.75
			36.7	12.9	24.4	8.9	0.68
1.5	0.107	18	49.5	27.8	20.2	8.9	0.55
			53.5	29.3	27.4	9.7	0.70
3.0	0.053	18	49.3	41.4	28.7	13.6	0.30
			51.9	39.5	27.8	14.2	0.62

Table I). Roughly linear relations are obtained as expected from physicochemical considerations.

Diffusion Study by Surface Extraction. The diffusion of methyl mercuric hydroxide into the fruit coat of wheat seeds was studied by surface extraction in a factorial experiment involving the storage time (five levels), the moisture content of the seed (two levels), and the volume of the disinfectant used in the treatment (three levels) as reported in Table III. Short storage times were chosen, because earlier studies (8) had indicated that diffusion is rapid, particularly at high moisture content. The seed disinfectants were experimental Panogen formulations containing methyl mercuric hydroxide with 0.8, 1.5, and 3.0% (weight by volume) mercury. Twelve 100-gram batches were treated on the same occasion and samples were taken for surface extraction from these batches at the times indicated in Table III.

Table III shows the very strong influences of storage time and moisture content. There is also an indication of slightly larger E values at the smaller volume dosages of seed disinfectant. A tendency in this direction is anticipated, because the initial indiffusion may be influenced by the amount of liquid used. Diffusion should not be too rapid during

the mixing process in the seed treater, to facilitate the spreading processes. (This was one main reason for the success of the Panogen process when this process was substituted for short wet treatment where larger liquid volumes were used.)

The liquid volumes used in this study are, however, so small that the influence on resorption, if any, is expected to be of no practical importance. The analysis of variance reported in Table IV was performed mainly to test the null hypothesis of no volume effect. Here logarithms are used to transform the distribution of the differences between the duplicates to a normal distribution and furthermore to reduce the strong interaction term between moisture content and storage time. (E is roughly proportional to $1/\sqrt{t}$. Transformation of E = const. $\times$ $1/\sqrt{t}$ to log E = log const. $-\frac{1}{2}$ log t eliminates this interaction.) Weakly significant effects are found for the volume factor, whereas moisture content and storage time are strongly significant factors.

The final treatment of the experimental results is done in Table V, where Z and the diffusion parameter, W, are evaluated as outlined in the section on theory. The three volume levels are pooled here, because the variations between these were comparatively small. The quantity KM, equal to E in

case all applied mercurial is still present in the extraction zone, was taken as 67.0 γ of mercury, which is the initial value for the low moisture level. This reference value was also used for the calculations based on the high moisture data, where diffusion is so rapid that no adequate initial value could be determined; some mercurial is evidently diffusing out of the extraction zone during the mixing process. The partition coefficient, K, is believed to be independent of the original moisture content, at least at short storage times, because the extraction zone is virtually soaked by water in the extraction procedure. For the same reason the extraction depth, h, is assumed constant.

Figure 3 shows Z calculated by means of Equation 4 as a function of $\sqrt{1/t}$. The high moisture data yield a fairly straight line over the large time interval studied—5 minutes to 1 month—in harmony with the theory. The different course observed for the low moisture data is probably due to interferences caused by the extraction procedure. Because diffusion is so much more rapid at a higher moisture content, it will be stimulated during the extraction moment. This effect is particularly pronounced for short storage times, when a large fraction of the mercurial is still present in the extraction zone prior to extraction. The Z values for the low moisture seeds at t = 35 minutes and 2 hours actually correspond to storage times of t = 2 and 3 minutes, respectively, in case of the high moisture seeds (Table V and Figure 2). Accelerated diffusion during the extraction procedure, which requires 4 minutes, is therefore a reasonable explanation to the nonlinear course of the low moisture curve in Figure 3.

The quantity W reported in Table V is consequently reasonably constant for the high moisture seeds but decreases markedly with time for the low moisture seeds. The W value for the longest storage time is, however, believed to be characteristic for the diffusion process itself, because the contribution of "extraction-induced diffusion" is here comparatively small.

Averaged data for seeds with 12% moisture from Table I yield results similar to those in Table V with W = 44 × 10⁻⁶ for t = 1 day; W = 2.6 × 10⁻⁶ for t = 1 week; and W = 2.1 × 10⁻⁶ for t = 1 month (the reference initial extractability was here assumed the same as in Table III).

The very strong influence of moisture content on the rate of diffusion is demonstrated by the fact that W for the 18% moisture seeds is larger than the 12% moisture seeds by a factor of 500 (Table V). As W = $\{D/(R + 1) \times (1/h)^2\}$ this increase may be caused by increase of D and/or decrease of R and/or h. The extraction depth, h, is believed to be essentially constant—increased moisture

content would rather increase than decrease h. R may be decreased at a high moisture content because of hydrolysis of complexes formed between the mercurial and reactive sites present in the fruit coat. Furthermore, increased moisture content is likely to have a profound influence on D, so that diffusion conditions will approach those in the aqueous phase. The 500-fold increase of W noted in Table V is thus probably due to increased D and decreased R.

The constancy of W indicates that the diffusion model used is satisfactory at least for the high moisture seeds. This would also imply that diffusion is taking place in an infinite medium, whereas it has been conclusively shown

that diffusion stops at the endosperm (7, 8). To explain this it is necessary to assume that more pronounced immobilization is taking place deeper in the fruit coat. Mercurial will then diffuse out of the extraction zone in much the same way as if in contact with an infinite medium.

The apparent diffusion constant, D, $(R + 1)$, cannot be evaluated, because h is not known. h is, however, necessarily smaller than the thickness of the fruit coat, which is about 0.01 cm. for wheat seeds. Table VI reports figures for $D/(R + 1)$ calculated for various estimates of h. Possible values for $D/(R + 1)$ are apparently much smaller than for diffusion of methyl mercuric

Table IV. Analysis of Variance of ¹⁰Log E Data from Table III

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F ratio	Significance
Dosage	2	0.4047	0.202	8.4	$P < 0.005$
Moisture content	1	5.2215	5.222	217	$P < 0.005$
Storage time	4	13.3728	3.343	139	$P < 0.005$
Moisture content × storage time	4	2.3470	0.587	24	$P < 0.005$
Storage time × dosage	8	0.2611			
Dosage × moisture content	2	0.0617			
Moisture content × storage time × dosage	8	0.1101			
Duplicates	30	0.3673	0.0122	(1/1.98)	$(P \sim 0.10$, none)
Total	59	22.1462			
Error estimate (combined interaction terms except moisture content × storage time)	18	0.4329	0.0241		

Table V. Evaluation of Diffusion Parameter for Wheat Seeds Treated with Experimental Panogen Formulations Containing Methyl Mercuric Hydroxide

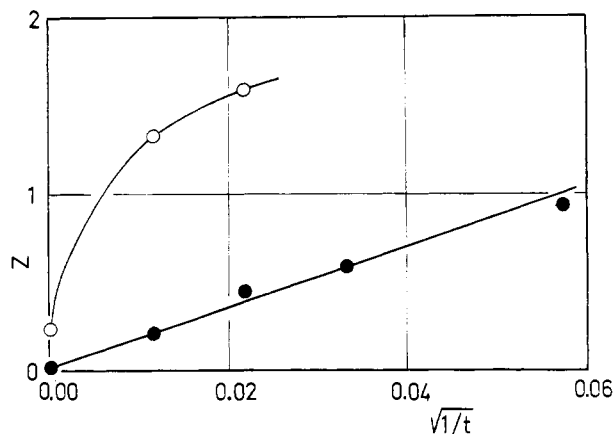| Moisture Content of Seed, %	Storage Time, Sec.	Av. E, γ Hg	E/KM $\{ = 2 \times \phi(Z)\}$ (Eq. 4)	Z (Eq. 4)	$W = \dfrac{D}{(R + 1) \times h^2}$ $\{= 1/(Z^2 \times 2t)\}$ (Eq. 5)
12	300	67.0	1.00	...	...
	900	68.0	1.01	...	...
	2100	59.5	0.888	1.59	94 × 10⁻⁶
	7500	54.5	0.813	1.32	38 × 10⁻⁶
	2.68 × 10⁶	12.8	0.191	0.241	3.2 × 10⁻⁶
18	300	43.7	0.652	0.938	1.9 × 10⁻³
	900	29.7	0.443	0.587	1.6 × 10⁻³
	2100	23.1	0.345	0.447	1.2 × 10⁻³
	7500	11.0	0.164	0.207	1.6 × 10⁻³
	2.68 × 10⁶	0.60	0.009	0.011	1.5 × 10⁻³

Figure 3. Test of diffusion model with $Z \equiv h \sqrt{(R + 1)/(2tD)}$ plotted as a function of $\sqrt{1/t}$ according to Equation 4

● 18% moisture seeds
○ 12% moisture seeds

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

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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-