

affected importantly by type of soil, since given sufficient time for diffusion, there was no perceptible difference between soils.

Relative effectiveness of Zn EDTA in the Sagemoor soil was about three times as great as in the Lakeland soil during early growth. With increased uptake from zinc sulfate in late growth, relative effectiveness of the chelate decreased sharply in either soil, but remained greater in the Sagemoor soil. The Sagemoor soil sorbs free zinc ions strongly, as evidenced by the low uptake of applied zinc. The chelate opposes this action by providing anionic zinc, which is not as greatly affected by sorption processes of soils. In view of these conditions, a zinc chelate may be expected to be relatively most effective in a soil having high affinity for cationic zinc.

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ZINC CARRIERS FOR CROPS

Preparation of Zinc Silicate Glasses for Experimental Use in Agriculture

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The influence of method of preparation and composition of 24.1% zinc (30% ZnO) glasses on the release of zinc to ammonium acetate, pH 4.0, was determined. Within the useful range of composition, the release of zinc from frits (unstirred melts) was greater, and less sensitive to differences in composition, than that from homogeneous glasses (stirred melts or remelts). Zinc release from frits was the same whether they were quenched on a dry steel surface or in water. Sodium-zinc glasses of satisfactory reactivity had compositions corresponding to $2 \text{ ZnO} \cdot \text{SiO}_2$ and $\text{Na}_2\text{O} \cdot n\text{SiO}_2$, where $n = 2$ to 3. The substitution of equimolar amounts of potassium oxide for sodium oxide or alumina for silica had no effect on the reactivity of frits.

GLASS carriers have been utilized in soil treatment to supply micronutrients slowly during growth of crops (2, 3). The glasses, like soil minerals, release their micronutrient constituents as they are degraded by weathering. In crop research directed toward the fundamental implications of this natural process, it is essential that rate of dissolution from an experimental glass be neither too slow nor too rapid. Otherwise, the results obtained will cast little, if any, light on the characteristics or potential value of a slowly soluble material.

The use of a glass containing only one micronutrient provides specificity needed in the interpretation of vegetative data. Zinc glasses of this type were made for use in a greenhouse experiment, the results of which have been reported (7). The reactivity of these glasses in relation to their method of preparation and composition is described in this article.

Experimental Procedure

Preparation of Glasses. Materials used in making the glasses were quartz flour and finely divided reagent grades of zinc oxide, sodium carbonate, potassium carbonate, and aluminum oxide.

The required amounts were formulated to obtain 20- to 25-gram samples of glass containing 24.1% of zinc (30% ZnO). In each of five series, one alkali oxide component was varied at the expense of silica, while other components were held constant. All formulations were mixed thoroughly, placed in a platinum crucible, and melted in a muffle furnace equipped with Globar elements. The temperature of the furnace was increased slowly to a few degrees above the point of fusion (900° to 1600° C.) and held at that temperature for at least one hour.

The following variants in procedure were used in the preparation of a series

Table I. Molar Compositions of 70% (Na₂O + SiO₂) . 30% ZnO Glasses within Useful Range of Reactivity

Ammonium Acetate-Extractable Zn, % of Total	Constituents, Moles 100 G. of Glass			SiO ₂ - 1/2 ZnO ^a Na ₂ O
	Na ₂ O	SiO ₂	ZnO	
		Frit		
10	0.239	0.919	0.369	3.1
40	0.290	0.867	0.369	2.4
70	0.340	0.814	0.369	1.9
		Homogeneous Glass		
10	0.307	0.848	0.369	2.2
40	0.325	0.830	0.369	2.0
70	0.339	0.816	0.369	1.9

^a 1/2 ZnO subtracted to exclude molar equivalent of SiO₂ in form of Zn₂SiO₄.

Table II. Ratio of Acidic to Basic Oxides in Zinc Frits at Different Levels of Reactivity

Type of Frit	Constituents of Frit, Mole %							
	Basic Oxides (B)				Acidic Oxides (A)			
	Na ₂ O	K ₂ O	ZnO	Total	SiO ₂	Al ₂ O ₃	Total	A/B
10% Ammonium Acetate-Extractable Zinc								
70% (Na ₂ O + SiO ₂).30% ZnO	15.7	...	24.2	39.9	60.2	...	60.2	1.51
62% (Na ₂ O + SiO ₂).30% ZnO.- 8% Al ₂ O ₃	14.9	...	25.1	40.0	54.8	5.3	60.1	1.50
70% (K ₂ O + SiO ₂).30% ZnO	...	13.5	25.9	39.4	60.6	...	60.6	1.54
64% (K ₂ O + SiO ₂).30% ZnO.- 6% Na ₂ O	6.6	7.6	25.1	39.3	60.7	...	60.7	1.54
62% (K ₂ O + SiO ₂).30% ZnO.- 8% Na ₂ O	8.7	6.1	25.0	39.8	60.2	...	60.2	1.51
40% Ammonium Acetate-Extractable Zinc								
70% (Na ₂ O + SiO ₂).30% ZnO	19.0	...	24.2	43.2	56.9	...	56.9	1.32
62% (Na ₂ O + SiO ₂).30% ZnO.- 8% Al ₂ O ₃	19.1	...	25.1	44.2	50.5	5.3	55.8	1.26
70% (K ₂ O + SiO ₂).30% ZnO	...	17.4	26.4	43.8	56.2	...	56.2	1.28
64% (K ₂ O + SiO ₂).30% ZnO.- 6% Na ₂ O	6.7	11.2	25.6	43.5	56.5	...	56.5	1.30
62% (K ₂ O + SiO ₂).30% ZnO.- 8% Na ₂ O	8.9	9.2	25.4	43.5	56.6	...	56.6	1.30
70% Ammonium Acetate-Extractable Zinc								
70% (Na ₂ O + SiO ₂).30% ZnO	22.3	...	24.2	46.5	53.5	...	53.5	1.15
62% (Na ₂ O + SiO ₂).30% ZnO.- 8% Al ₂ O ₃	21.9	...	25.1	47.0	47.7	5.3	53.0	1.13
70% (K ₂ O + SiO ₂).30% ZnO	...	18.8	26.6	45.4	54.6	...	54.6	1.20
64% (K ₂ O + SiO ₂).30% ZnO.- 6% Na ₂ O	6.8	13.1	25.9	45.8	54.2	...	54.2	1.18
62% (K ₂ O + SiO ₂).30% ZnO.- 8% Na ₂ O	9.0	11.7	25.7	46.4	53.6	...	53.6	1.16

of 70% (Na₂O + SiO₂).30% ZnO glasses:

A. Quenching an unstirred melt in a dry stainless steel beaker

B. Quenching an unstirred melt in cold water

C. Quenching an unstirred melt in a dry stainless steel beaker, pulverizing it in a steel mortar, remelting the glass, and quenching it as before

D. Stirring a 1-pound melt for several hours and pouring it into a steel form

Procedure A was adopted as the standard method for preparing other glass compositions.

A Mikro-samplmill (Metals Disintegrating Co., Inc.) was used for final grinding of the glass. The sieve analysis of a typical sample after grinding was 7.3% 20- to 48-mesh, 32.3% 48- to 100-mesh, 32.9% 100- to 200-mesh, and 27.4% passing 200-mesh. Some metal

was abraded from the stainless steel hammers and liner of the mill, but tests with glasses containing no zinc showed that the contaminating metal had no effect on the determination of extractable zinc.

Determination of Chemical Reactivity. A 1-gram sample of the 48- to 200-mesh glass and 40 ml. of ammonium acetate, pH 4.0 (2N acetic acid plus ammonium hydroxide), were placed in a celluloid centrifuge tube and rotated for 16 hours on an end-over-end agitator. At the end of the extraction period, the solution was centrifuged, and an aliquot of the supernatant liquid was taken for the determination of zinc by titration with potassium ferrocyanide (4).

Influence of Method of Preparation

All of the 70% (Na₂O + SiO₂).30% ZnO melts were clear, colorless, and

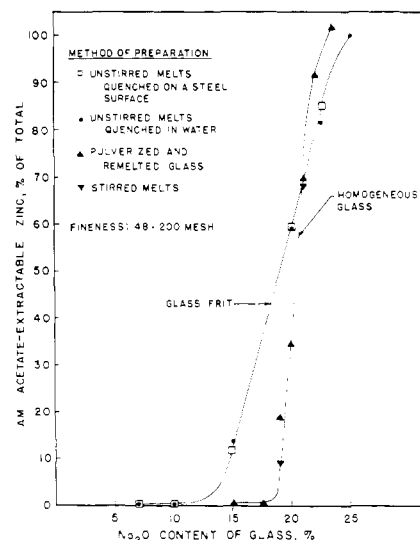


Figure 1. Effect of method of preparation on reactivity of 70% (Na₂O + SiO₂) . 30% ZnO glasses

somewhat viscous liquids. Petrographic examination of the materials after solidification showed that they were all glass in physical form. The preparations made in single unstirred melts may be identified as "frits," since the procedure was similar to that used in the manufacture of commercial frits. The products from pulverized and remelted frits and from stirred melts are regarded as homogeneous glasses; those of the stirred melts were identified as such by usual optical methods. The amounts of zinc extracted from these materials by ammonium acetate, pH 4.0, are shown in Figure 1 in relation to sodium oxide formulation.

The release of zinc from the frits was not affected by method of quenching. The more rapid cooling in water shattered the frits, but possible differences in molecular structure and internal stress were not reflected in chemical reactivity of the ground product.

The increased molecular homogeneity, obtained by stirring the melt or by remelting a pulverized frit, was accompanied by a sharp change in chemical reactivity. As indicated in Figure 1, the glasses were more reactive above 70% zinc release to ammonium acetate than frits of the same composition, and less reactive than frits below this level of release. The differences above 70% release are of little consequence, since the optimal range for agricultural use (before reduction to the required fineness) lies between about 10 and 70% release. Compared with the frit at 40% release the identical composition of homogeneous glass released only about 1% of its zinc to ammonium acetate.

In view of this circumstance, consistency with respect to the amount of

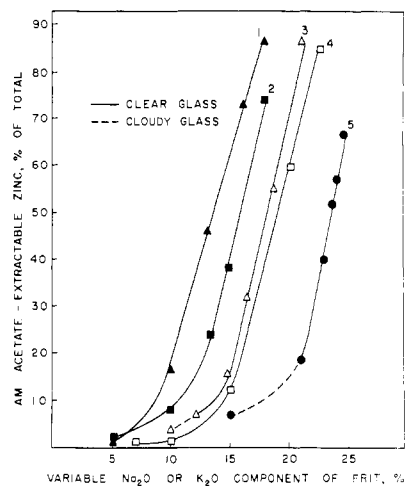


Figure 2. Influence of composition on reactivity of zinc frits

1. 62% ($K_2O + SiO_2$).30% ZnO .8% Na_2O
2. 64% ($K_2O + SiO_2$).30% ZnO .6% Na_2O
3. 62% ($Na_2O + SiO_2$).30% ZnO .8% Al_2O_3
4. 70% ($Na_2O + SiO_2$).30% ZnO
5. 70% ($K_2O + SiO_2$).30% ZnO

mixing during the molten stage is important in making a glass for agricultural purposes. Homogeneity of the glass at a given level of reactivity has not been shown, in itself, to affect vegetative results. However, the procedure for

making a frit is simpler, since the melt is not stirred or otherwise mixed. The preparation of frits is also preferred because their reactivity is less affected by differences in composition.

Influence of Chemical Composition

The molar compositions of suitable sodium-zinc glasses are given in Table I. To define the type of material, zinc in the glass is arbitrarily assigned the composition of Zn_2SiO_4 , the only known silicate of zinc (5). The ratio of the matrix silica (excess of that in the form of Zn_2SiO_4) to sodium oxide content varied from 1.9 to 2.2 with homogeneous glasses and from 1.9 to 3.1 with the frits. Hence, these materials may be characterized as solutions consisting of $2ZnO \cdot SiO_2$ and $Na_2O \cdot nSiO_2$, where n has the value of about 2 to 3.

The release of zinc from frits containing potassium or aluminum is compared with that from the sodium frit in Figure 2. The frits were clear glass, except in a few cases at low reactivity, as depicted by broken line segments of the curves. Within the useful range of reactivity, the curves are nearly parallel. Thus, the sensitivity of zinc release to differences in composition was much the same for each type of frit.

The molar ratio of the acid and basic constituents largely determined reactivity of the frits, as shown by the data

in Table II. At a given level of reactivity, the ratio of "acidic" oxides (SiO_2 and Al_2O_3) to basic oxides (Na_2O , K_2O , and ZnO) was sensibly constant. Potassium oxide merely replaced sodium oxide, and alumina replaced silica with little or no effect on the release of zinc.

Acknowledgment

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FERTILIZER ANALYSIS

Quantitative Analysis of Mixed Fertilizers by X-Ray Diffraction

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An x-ray diffraction method is described by which the compounds in mixed fertilizers are identified and their amounts determined quantitatively. Spinel ($MgAl_2O_4$) serves as an internal standard. The method is sufficiently accurate to yield practical information on the mineralogical composition of mixed fertilizers, and results are reported of the analyses of typical fertilizers.

KNOWLEDGE of the mineralogical composition of a mixed fertilizer is a great help toward understanding the reactions involved in its manufacture, its caking during storage, and its behavior in the soil. Chemical analysis yields little information on the actual compounds in a complex mixed fertilizer, and petrographic examination is hampered, considerably more than are x-ray methods, by the colloidal and gelatinous materials present in many mixed fertilizers.

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Development of Method

Ando and Matsuno (1, 2) adapted the quantitative x-ray diffraction method of analysis (3, 4) to fertilizers. Spinel ($MgAl_2O_4$) served as an internal standard; its diffraction peaks are relatively free of interference from those of many of the compounds in mixed fertilizers, the intensity of its principal peak is virtually unaffected by the grinding required in preparing samples for examination, it has a moderate x-ray absorption coefficient, and it is inert to the common fertilizer components.

The procedure based on spinel was developed further and applied to the analysis of different types of fertilizers. Calibration curves were made for some 20 compounds and several solid solutions often present in mixed fertilizers. Interferences of diffraction peaks of the compounds with those of spinel were identified, and corrections were made. The method yields dependable information on the mineralogical composition of mixed fertilizers, and the results are in reasonable agreement with those of chemical analyses.