GLASS AS A BORON SOURCE

Relationship of Surface Area and Particle-Size Distribution of Borosilicate Glasses to Boron Status of Alfalfa

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The effect of varying particle size of slowly soluble borosilicate glasses on crop boron was investigated in a greenhouse experiment by growth of alfalfa from Evesboro soil to which the test materials were added. Boron content in all harvests of the crop varied directly with specific surface area of a glass having low chemical reactivity. As the chemical reactivity of the glasses increased, peak effectiveness shifted from the finest to the intermediate and then to the coarsest sieve fractions of glass. Peak effectiveness also shifted, more or less gradually, to coarser particles of glass as the length of time in the soil increased. Uniformly sized particles of moderately reactive glasses had greater ability to minimize seasonal variation in crop boron than comparable nonclassified particles.

Release from a slightly soluble borosilicate glass of as little boron as that equivalent to about 0.6 pound of borax per acre within a deficient soil increases the alfalfa yields significantly (*1*). No tendency of such a glass to produce boron toxicity was observed even at exceedingly high levels of application. The residual glass releases boron steadily during subsequent seasons, thereby compensating for losses of soluble boron from the soil (*2*). Certain more reactive glasses are better suited to the immediate needs of the crops (*4*). Glass carriers of this kind tend to minimize the seasonal variation of crop boron, and have a readily identifiable range of moderate reactivity wherein boron present in the glass is utilized most efficiently (*3*).

This paper reports a study of the effects of varying fineness of boron glasses (frits) on the growth and boron content of consecutive harvests of Ranger alfalfa, when grown from Evesboro sandy loam cultures under greenhouse conditions. Borax was used as the standard of comparison. Physical conditions, procedures, and chemical compositions of the test materials were those described earlier (*3*). The results are interpreted in terms of surface area and particle size.

Experimental

The glass fineness was varied by treating the soil with classified particles, differing in sieve size, and with nonclassified particles, differing in the length of time ground in a porcelain ball mill. The sieve fractions were those of glasses 176-B, -E, and -C, in order of decreasing chemical reactivity—relative ability to release boron at equal fineness. The simple multiples of change in "unit" particle diameter and specific surface of these preparations are given in Table I. The grinds consisted of the −20-mesh material (passing through a 20-mesh sieve) of glasses 176-B, -E, -F, and -C, ground either for 0.5 or 2 hours. The mill fineness of each grind is characterized by a sieve analysis (Table II).

Glass 176-C used in the present work is a recent preparation intended to duplicate a lot used in previous studies (*1–4*). Although the chemical analyses are nearly the same, the new lot showed a much higher reactivity.

The glasses were mixed, individually, with the limed and fertilized soil in amounts equivalent to 10, 20, and 40 pounds of borax per acre. Borax, containing 36.52% of boron trioxide, was applied in a parallel series of 5, 10, 20, and 40 pounds per acre.

Coefficients of variation with respect to the means of the triplicated treatments in separate harvests were 5.7 ± 1.2% for yield and 7.3 ± 1.6% for the boron content of the crop.

Vegetative Response

The controls with no added boron usually exhibited boron deficiency symptoms. All applications of either glass or borax produced normal, healthy alfalfa and increased the forage yield. Significant differences in yield between boron treatments and controls first appeared in the third harvest, became progressively greater in the fourth and fifth harvests, and then decreased somewhat in the sixth. The yield was unaffected by differences in carrier type or application. Average results for yield are given in Table III.

Influence of Classified Particles on Crop Boron

Relationship to Specific Surface of Glass. The influence of sieve fineness on the boron content of the crop (Table IV) was, in general, similar at different levels of application. However, at the 10- and 20-pound level applications the boron contents were often within a low range, wherein the response to the applications of the soluble boron (Table V) was decidedly nonlinear. At the 40-pound level application, the higher response levels of the glass treatments were always within the region of near-linear response to soluble boron. In view of this circumstance, the relationship of crop boron to the surface area of the glasses may be considered with advantage at the 40-pound level, as depicted in Figure 1.

At high application, the boron content of the crop varied linearly with the surface of the least reactive glass, No. 176-C, in the first four harvests. While the boron contents drop successively in these harvests, those of the glass treatments rise in position relative to the respective levels obtained in the equivalent borax treatment (horizontal broken lines in Figure 1). With this gradual relative rise, the boron contents at high surface become greater than those of the borax treatment in the third and following harvests. In the last two harvests, the rise, though continuous at low and intermediate surfaces, slowed greatly at high surface, thereby producing a curvilinear relationship. However, release of soluble boron from the glass was presumably continuous at high surface, because response to the glass remained well above that to borax. These results show that the boron solubilized steadily from glass 176-C throughout a period of 9 months.

The effect of a more chemically reactive glass, No. 176-E, on crop boron in the first harvest was proportionately very similar to that of glass 176-C in the last harvest. Approximately the same stage of total boron release was reached by glass 176-E during the 2-month period prior to the first harvest as was reached by glass 176-C during the 9-month period prior to the sixth harvest.

The typical pattern of curve change which occurred as glass 176-E reacted with the moist soil is well illustrated by the 40-pound treatment. In the first harvest, crop boron increased with surface of the glass, and exceeded that of the equivalent borax treatment at high surface. In subsequent harvests, the curves bend as crop boron dropped steadily at high surface and rose at low surface. Through this relative movement, the curves become arch-shaped with the intermediate fineness producing the highest levels of boron in the crop. The curve rotation, so effected, continues at a greatly reduced rate in late harvests, and, in the last two harvests, the coarsest glass tended to produce somewhat higher levels in the crop than the most finely divided glass.

The effect of the most reactive glass in the series, No. 176-B, on crop boron in the first harvest was, proportionately, very similar to that of 176-E in the last harvest. Because this relationship is similar to that which 176-E bears to 176-C, the multiple change in chemical reactivity was of the same order of magnitude.

The arched curve of the first harvest shows that the influence of glass 176-B on crop boron was greatest at intermediate levels of surface during the first 2 months. After this period of rapid solubilization, an inverse relationship is exhibited with the low surface glass producing the highest boron contents in the crop. The reversion of the curves to an archlike shape in late harvests at the high level of application (Figure 1) did not occur at low application. The small differences in this case appear to be relatively unimportant, and their causes are uncertain.

Early Response Relatively High at Low Application. In the first one or two harvests, the results for the three glasses show an interesting similarity in the variation of the response with the amount of applied boron (Table IV). Crop boron in glass treatments, relative to that in corresponding borax treatments (Table V), was proportionately greater at low application. This tendency, if generally the case, offers some protection to the crops during their early growth by the partial compensation obtained when applications are either higher or lower than optimal for the crop.

Effect of Varying Reactivity. The broad effect of varying the reactivity of glass carriers on crop boron, through changes in sieve fineness, is illustrated in Figure 2. With increased fineness, the more or less parallel response curves of glass 176-C rise into the range of moderate reactivity, in which glasses produce lower boron contents in early harvests and higher boron contents in late harvests than equivalent applications

Table I. Multiple Change in Mean Particle Diameter and Specific Surface of Sieve Fractions

Glass, Mesh Size: Treatment	Glass, Mesh Size: Partitioning half-interval	Unit Diameter, 1 = 37 μ	Unit Surface 1 = 136 Sq. Cm./G.[a]
−200		1	6
	200	2	3
100 to 200		3	2
	100	4	1.5
48 to 100		6	1

[a] Calculated from arithmetic mean of sieve openings, assuming uniform spheres with a density of 2.

Table II. Fineness of the —20-Mesh Glasses

Glass	Grinding Time, Hours	Glass Retained between Mesh Sizes, % of Total: 20 to 48	48 to 100	100 to 200	−200
176-B	2	5.1	24.4	25.9	45.2
	0.5	40.1	28.9	15.2	15.9
176-E	2	4.8	23.7	25.9	45.6
	0.5	38.8	28.9	15.4	16.9
176-F	2	2.4	19.8	27.6	50.2
	0.5	40.8	28.0	14.2	17.0
176-C	2	4.1	23.3	26.0	46.8
	0.5	39.2	29.3	15.1	16.4

Table III. Influence of Boron Fertilization on Alfalfa Yields

Carrier Type	Treatment[a]: Boron added to soil, borax equiv., lb./acre	Treatment[a]: Number of triplicated treatments	Average Yield of Consecutive Harvests, Grams/Culture[b]: 1	2	3	4	5	6
None		2	2.73	2.84	2.53	2.60	3.55	4.48
Borax	5 to 40	4	2.84	3.09	3.11	3.62	5.30	5.70
Glass	10 to 40	51	2.68	2.91	3.13	3.59	5.23	5.63

[a] Neither carrier type nor application had any significant effect on yield.
[b] Oven-dry weight, 65° C.

Table IV. Effect of Fineness of Uniformly Sized Glass Particles on Boron Content of Alfalfa

Glass: Number	Glass: Mesh size	Boron Added to Soil, Borax Equiv., Lb./Acre	Boron Content of Consecutive Harvests, P.P.M.: 1	2	3	4	5	6
176-B	−200	10	70.3	39.0	30.0	23.0	18.9	33.6
		20	96.0	60.8	42.1	32.8	26.8	42.4
		40	134.2	89.5	67.8	51.9	42.7	72.1
	100 to 200	10	75.6	44.6	30.6	25.2	19.4	29.3
		20	111.4	66.4	43.3	33.7	24.6	39.9
		40	150.0	84.2	69.5	57.1	44.1	74.5
	48 to 100	10	71.5	47.1	36.4	26.3	21.1	33.7
		20	102.4	74.4	46.3	38.9	29.3	35.8
		40	146.0	112.8	83.0	63.7	40.3	64.8
176-E	−200	10	65.7	43.7	29.3	22.6	18.5	37.7
		20	97.4	58.8	42.7	33.4	25.2	37.9
		40	160.2	112.0	75.0	58.6	40.4	72.5
	100 to 200	10	70.6	46.3	31.8	28.7	24.1	39.8
		20	94.0	65.1	49.5	38.3	37.0	52.9
		40	122.2	100.2	85.0	67.6	54.6	98.4
	48 to 100	10	53.5	37.2	29.9	27.1	23.0	30.0
		20	70.7	55.0	42.4	37.9	35.2	43.7
		40	94.7	76.6	68.9	53.1	50.3	75.4
176-C	−200	10	59.7	40.0	32.0	26.9	23.9	31.6
		20	76.2	57.0	44.1	35.5	32.9	44.8
		40	110.9	89.5	82.6	70.7	61.0	85.7
	100 to 200	10	40.6	32.8	24.1	24.1	22.0	27.6
		20	51.7	42.6	30.2	24.3	27.9	40.4
		40	66.7	51.4	44.9	36.3	40.5	61.2
	48 to 100	10	27.8	19.0	17.6	15.9	13.2	26.1
		20	40.5	28.5	27.1	21.3	18.9	35.5
		40	54.2	41.0	34.9	27.0	24.8	42.2

of borax. The general rise with increased fineness also took place in the case of the two coarser fractions of the more reactive glass 176-E. However, when the fineness was increased to −200-mesh, the further increase in early harvests was accompanied by a decrease in late harvests. Through this change, the influence of the glass became similar to that of borax.

Effectiveness of Sieve Fractions

Relationship to Reactivity. The relative ability of glass carriers to supply boron to the crop may be isolated from normal seasonal variation, and placed on a basis suitable for averaging, by computing relative effectiveness of the treatments in terms of the ratio of borax application to glass application at equal response in boron content of the crop. The average ratio for the three levels of application of each glass is plotted with respect to time in Figure 3. By reference to the direction of curve displacement with increased fineness—vertical arrows—and comparison of general levels of effectiveness, the order of increasing reactivity may be determined, as indicated by numbering the curves from 1 to 9. In this order, effectiveness increased from curves 1 to 5 in all harvests. From curves 5 to 6, effectiveness increased somewhat further in the first three harvests, but decreased in the last three. Proceeding from curves 6 to 8, the values in the first five harvests show a small, but definite, general decrease. Finally, curve 9 is essentially the same as curve 8, indicating that a limiting value of the reactivity had been approached.

Minimization of Seasonal Variation. Effectiveness of the glasses, relative to borax, varied inversely with normal seasonal variation in the boron content of the crop. Hence, the relative ability of the glasses to minimize the variation of crop boron is indicated by the magnitude of maximum change in the relative effectiveness (Table VI). In descending from high to low reactivity, the maximum change increased from one, or little more, to approximately three.

Optimal Performance. By measuring the highest effectiveness obtained when the general levels of crop boron were the least—fifth harvest—and the ability to lower seasonal variation in crop boron, optimal performance was obtained with the −200-mesh glass of 176-C and the 48- to 100-mesh glass of 176-E. Average effectiveness of these materials was 0.8 ± 0.1 in the first two harvests, and greater than 1 in the following harvests. As reactivity of the glasses increased above this optimal level for single season use, ability to minimize seasonal variation (Table VI) decreased rapidly. Below this level, ability to minimize variation was sustained, but effectiveness was lower in all harvests.

Particle Size *vs.* Composition. No significant difference was observed to exist between the effect of varying particle size and that of varying composition. The similarity in the influence of these two variables is shown in Figure 3 by the parallelism of the results for the finely divided −200-mesh glass of 176-C (curve 4) and those for the coarse 48- to 100-mesh glass of 176-E (curve 3). At lower reactivity, the pattern of effectiveness with the 100- to 200-mesh glass of 176-C (curve 2) was much the same as that of the somewhat coarser 48- to 100-mesh glass of 176-F, previously described (*3*).

Particle Size in Moderate Range. Glasses having different compositions—or different physicochemical structures—will, ordinarily, have different finenesses within the range of moderate reactivity. Nevertheless, the ratio of the largest particle diameter to that of the smallest within this range should be the same for any glass. This definitive ratio may be estimated by relating the gradient changes in average effectiveness (Figure 3) to the respective changes in unit diameter (Table I).

The lower part of the range of moderate reactivity is traversed by glass 176-C. The lower limit at which effectiveness of the glass just began to exceed that of borax was about midway between curves 1 and 2. The optimal condition was reached in curve 4. These two

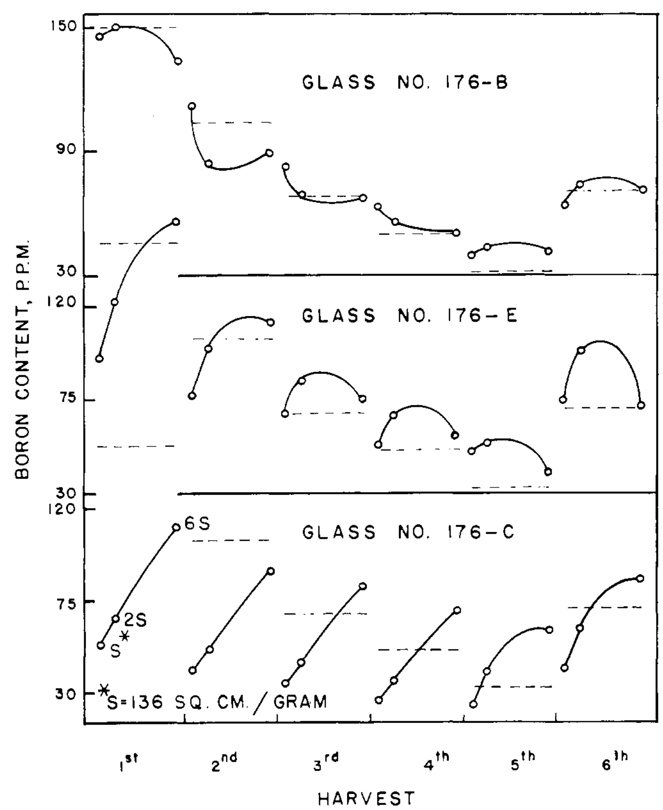

Figure 1. Relationship of initial surface area of glass carriers to boron content of alfalfa, and to the effect of borax (horizontal broken lines)

Application level equivalent to 40 pounds of borax per acre

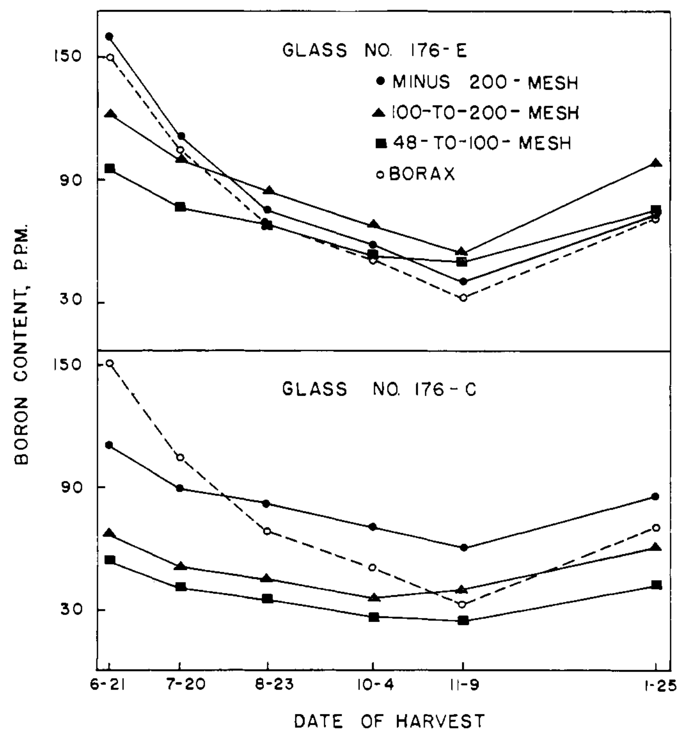

Figure 2. Effect of sieve fineness of glass carriers on boron content of alfalfa, and the relationship of the effect to borax

Application level equivalent to 40 pounds of borax per acre levels correspond to the 100-mesh and the −200-mesh materials, having unit diameters of 4 and 1, respectively. Thus, the multiple change in diameter was in the ratio of approximately 4 to 1.

The upper part of the range of moderate reactivity is traversed by glass 176-E and partially so by glass 176-B. The levels of effectiveness of glass 176-C in curve 4, taken somewhat arbitrarily to be optimal, were about midway between curves 3 and 5 of glass 176-E. As such, optimal fineness of glass 176-E may be said, for present purposes, to be 100-mesh which corresponds to a unit diameter of 4. The upper limit of the moderate range appears to be exceeded at −200-mesh with unit diameter of 1 in curve 8, as no further change occurred in curve 9. Hence, the ratio of change in diameter was less than 4 to 1 in this region. By similar comparison, curves 6 and 7 of glass 176-B indicate that the ratio of change was greater than 6 to 3 or 2 to 1. Thus, the intermediate ratio of 3 to 1 represents the approximate relationship of particle diameter from optimum to upper limit. This value combined with the ratio for the lower part of the range, 4 to 1, shows that the multiple change in particle diameter was about 12 to 1, within the limits of moderate reactivity.

Influence of Nonclassified Particles on Crop Boron

The effect of fineness of the grinds on crop boron, characteristic of the base data given in Table VII, is illustrated in Figure 4 by plotting the results for some of the glasses at the 40-pound level. In general, the relative influence on boron content of the crop was similar to that of the sieve fractions. In ascending from low to high reactivity, crop boron increased in all harvests from the 0.5-hour grind of 176-C to the moderate range with the 2-hour grind of 176-C and both grinds of 176-F (not illustrated) and 176-E. For the highly reactive glass 176-B, the 2-hour grind produced higher values in the first two harvests, but lower values in the third and following harvests, than the coarser 0.5-hour grind. Thus, the relative change at high reactivity was much the same as registered by the two finer sieve fractions of glass 176-E (Figure 2).

The salient points of difference between the results in the ground series and those in the sieve fractions may be discerned by comparing Figures 2 and 4. In the grinds, as illustrated by glass 176-E, the boron content of the crop tended to drop more steeply as early harvests were taken, and to be relatively lower in late harvests, especially in the fifth harvest, than in comparable sieve fractions. These differences, which vary complexly with degree of fineness and with other sources of variation, cannot

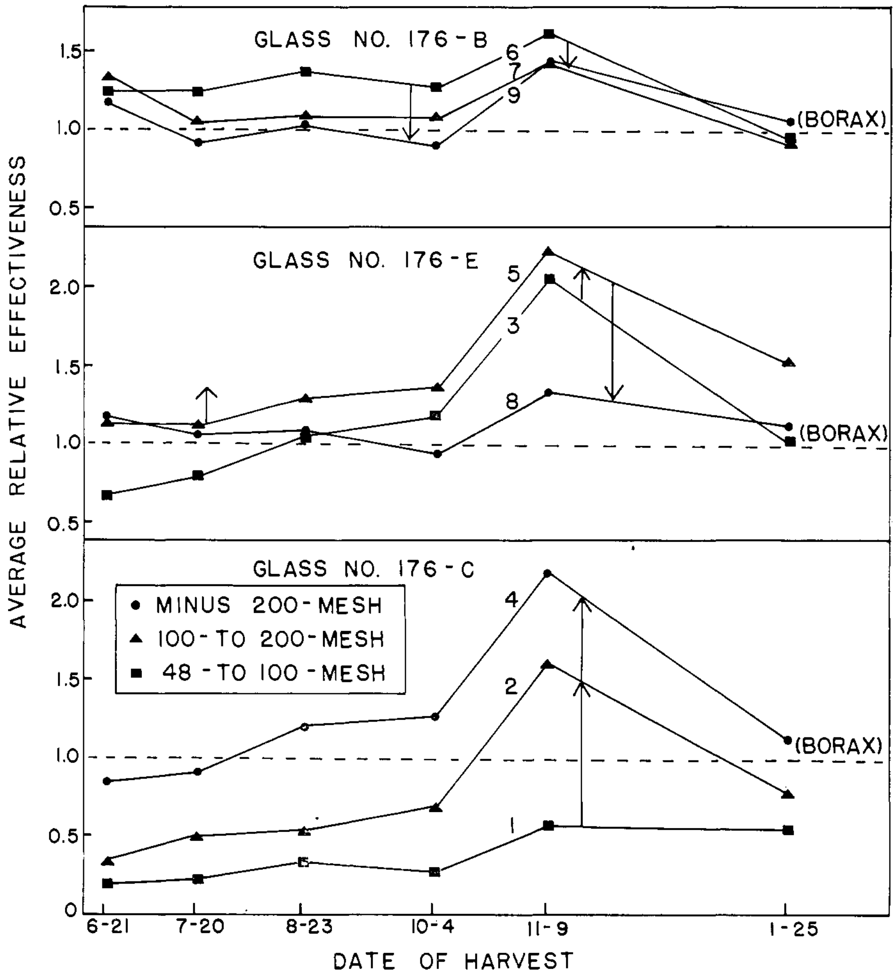

Figure 3. Relative effectiveness of sieve fractions

Numbers on curves indicate order of increasing reactivity

Vertical arrows show direction of change with increasing fineness

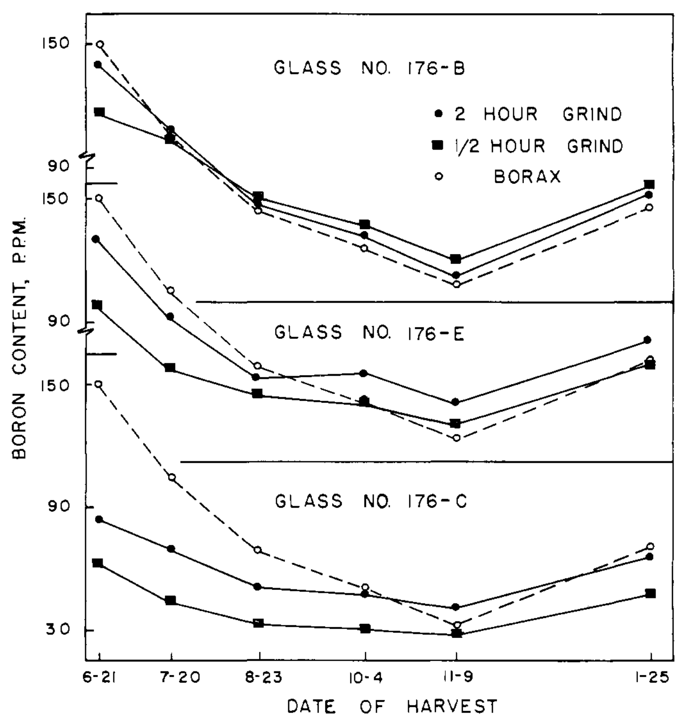

Figure 4. Effect of mill fineness of glass carriers on boron content of alfalfa, and the relationship of the effect to borax

Application level equivalent to 40 pounds of borax per acre

Table V. Effect of Readily Soluble Boron of Reference Material on Boron Content of Alfalfa

Borax Added to Soil, Lb./Acre	Boron Content of Consecutive Harvests, P.P.M. 1	2	3	4	5	6
0	15.8	12.9	12.6	8.9	9.5	15.3
5	48.5	29.8	24.9	21.9	14.9	26.9
10	60.0	42.3	29.0	23.7	16.5	30.6
20	83.7	59.1	40.6	35.1	22.0	43.6
40	151.0	104.6	69.2	51.6	33.0	71.3

Table VI. Relative Ability of Sieve Fractions to Minimize Seasonal Variation in Crop Boron

Glass			Maximum Change in Relative Effectiveness, Mean Ratio of 5th/1st Harvest	
Number	Mesh size	Reactivity	Fineness	Composition
176-B	−200	High	1.3	1.2
	100 to 200	High	1.1	
	48 to 100	High	1.3	
176-E	−200	High	1.1	2.1
	100 to 200	Moderate	2.1	
	48 to 100	Moderate	3.1	
176-C	−200	Moderate	2.7	3.5
	100 to 200	Moderate	4.8	
	48 to 100	Low	3.0	

Table VII. Effect of Fineness of Nonclassified Particles of Grinds on Boron Content of Alfalfa

Glass Number	Grinding time, hours	Boron Added to Soil, Borax Equiv., Lb./Acre	Boron Content of Consecutive Harvests, P.P.M. 1st	2nd	3rd	4th	5th	6th
176-B	2	10	61.4	48.2	28.8	23.1	16.3	30.6
		20	91.2	64.9	42.3	38.7	23.4	40.9
		40	140.9	109.6	72.7	56.9	37.4	77.1
	0.5	10	59.6	49.8	35.5	26.9	18.6	32.0
		20	83.8	60.6	47.1	39.4	26.8	44.7
		40	117.2	103.9	76.1	61.9	45.2	83.4
176-E	2	10	69.0	40.0	29.1	26.7	19.9	36.0
		20	80.8	57.4	41.6	37.1	26.8	44.5
		40	130.8	92.6	63.2	66.7	51.5	86.7
	0.5	10	55.6	28.7	25.0	19.7	17.5	29.5
		20	63.4	48.1	35.5	33.5	25.5	40.3
		40	99.0	67.9	55.6	51.4	41.4	70.4
176-F	2	10	58.8	38.3	27.1	22.4	21.1	37.7
		20	77.4	59.3	38.1	35.5	30.8	44 4
		40	103.3	82.1	61.1	56.3	46.0	74.4
	0.5	10	55.6	27.6	24.2	21.7	18.7	33.3
		20	70.7	41.5	32.4	30.0	25.3	44.2
		40	73.8	56.1	51.4	46.4	39.9	74.2
176-C	2	10	53.8	35.5	29.3	23.8	18.8	31.8
		20	68.7	49.0	38.0	29.6	24.3	44.2
		40	84.8	70.2	51.7	48.6	41.2	66.4
	0.5	10	40.9	22.8	19.6	16.1	17.6	26.7
		20	53.2	37.0	30.0	23.9	20.9	33.8
		40	63.6	44.4	34.0	31.6	28.3	47.8

Table VIII. Relative Ability of Grinds to Minimize Seasonal Variation in Crop Boron

Number	Glass Grinding time, hours	Reactivity	Maximum Change in Relative Effectiveness, Mean Ratio of 5th/1st Harvest Fineness	Composition
176-B	2	High	1.1	1.4
	0.5	High	1.6	
176-E	2	Moderate	1.6	1.8
	0.5	Moderate	2.0	
176-F	2	Moderate	2.1	2.2
	0.5	Moderate	2.3	
176-C	2	Moderate	2.1	2.5
	0.5	Low	2.8	

be assessed satisfactorily by direct reference to the base data.

Effectiveness of Grinds

Average effectiveness of each grind in successive harvests is depicted in Figure 5. The results, when considered from this standpoint, differ from those of sieve fractions (Figure 3) in that the rise in effectiveness during the season was not as rapid and the peak values reached were not as great.

The more gradual rise in effectiveness with time reflects the fact that the nonclassified particles of the grinds had less ability to minimize the seasonal variation in crop boron. By general average, the ratio of maximum change in effectiveness, serving as a measure of this property, was 2.0 for grinds (Table VIII) as compared to 3.2 for sieve fractions (Table VI) within the range of moderate reactivity. As such, the advantageous increment over borax—each ratio minus one—was only one half as great as that obtained with uniformly sized particles.

The lower peak values, occurring in the fifth harvest when boron contents were the least, show that the grinds, although superior to borax, corrected deficiency less than comparable sieve fractions. Within the range of moderate reactivity, the general average of effectiveness at this time was 1.5 for grinds as compared to 2.0 for sieve fractions. Hence, the advantageous increment over borax (effectiveness minus one) was again only about one half as great as that obtained with uniformly sized particles.

Maximum performance with respect to these two aspects of behavior did not overlap in the grinds, as it did in the series of sieve fractions. The 2-hour grinds of 176-E and -F produced the highest levels of effectiveness in the fifth harvest. The respective mean ratios of maximum change in effectiveness were 1.6 and 2.1. By comparison, the highest obtainable ratio of about 3.0—under the conditions of this experiment—was not closely approached until the reactivity of the glasses dropped to the low level of the 0.5-hour grind of glass 176-C, in which case the mean ratio was 2.8. Thus, as the reactivity was varied, an increased benefit in one of the two properties was gained only at the expense of a loss in the other.

The underlying cause for the less efficacious results with the grinds is related to their wide spans in particle size. In each case, some of the particles contained in the grinds were not appropriately sized. The 48- to 100-mesh particles of glass 176-C were of low reactivity. In the 0.5- and 2-hour grinds, the material of this size or larger (Table II) represented 68.5 and 27.4% of the samples by weight, respectively. In other cases, the performance of the grinds was lowered by the presence of undersized particles. The −200-mesh glass 176-E was too highly reactive, because its influence on the crop boron was slightly different from that of borax. The amounts of −200-mesh material in the 0.5- and 2-hour grinds of this glass were 16.9 and 45.6% of the samples, respectively.

Influence of Glasses on Soluble Supply

Supernormal State Obtained. Boron contents of the crop in glass treatments during late harvests have been proportionately greater relative to those of equivalent borax treatments than could be explained satisfactorily in terms of corresponding differences in residual supply (*3*). This circumstance indicates that newly released boron is taken up more efficiently by a crop than a readily soluble form which has been completely free to equilibrate with the soil.

With the inclusion of several finenesses for each glass used, the existence of a supernormal state of soluble supply became more evident in a special case. At or close to the transition between moderate to high reactivity, the residual of the added boron after crop removal of each harvest was substantially the same in glass treatments as it was in equivalent borax treatments. Under this condition of equal total supply, the levels of boron in the crop were usually much greater with the glasses than with borax after the first two harvests (Figure 2, 100- to 200-mesh of glass 176-E and 200-mesh glass of 176-C; and Figure 4, 0.5-hour grind of 176-B and 2-hour grind of 176-E). In terms of average relative effectiveness, the performance of the glasses in late harvests ranged from 1.0 (for borax) upward to peak values of 1.4 to 2.2 (Figure 3, curves 4, 5, and 6; Figure 5, curves 6 and 7). The disappearance of the elevated response to the glasses at high reactivity, when the amounts of boron released after an early period would be negligibly small, indicates that this influence of glass carriers is largely dependent on the rate of release.

The presence of a supernormal state of soluble supply is not usually evident in early harvests or at low reactivity, when crop boron is limited materially by the low amounts of boron dissolved from a glass. However, it presumably exists in the early period or whenever boron dissolves slowly from a carrier. The tendency of the boron contents to form maxima with relation to surface area at some level of reactivity in each of the six harvests (Figure 1) strongly supports this view.

Dependency on Particle-Size Distribution. When particle size is reduced by grinding a glass until it becomes moderately reactive, a wide and more or less normal distribution curve of particle size is made to coincide approximately with the size range best suited to first year crop growth. As fineness is increased within this general range to obtain a more complete release of boron during the season, the amount of very fine material is increased mostly through a commensurate loss in the amount of very coarse material (−200-mesh and 20- to 48-mesh size, respectively, in Table II). The fine material dissolves rapidly and imposes little, if any, restriction on seasonal variation. Consequently, as total solubilization is increased by grinding, the glasses gradually lose their ability to minimize seasonal variation.

The failure of boron contents in late harvests of the grinds to become as great as those of sieve fractions relates to a lower rate of boron release. No matter what degree of fineness a grind may have, the amount of boron it will release during the latter part of the season will always be lower than that obtainable with uniformly sized particles. That portion of glass boron contained in very fine particles which dissolve completely, or nearly so, in the early part of the season will contribute little or nothing to the over-all rate of release thereafter. Boron contained in coarse particles with a low specific surface contributes much less to the rate of release than an equal amount of boron in smaller more ideally sized particles. Consequently, the rate-dependent supernormal state of the soluble supply during late harvests cannot be as great with grinds as that obtained with comparable sieve fractions. The resulting differences in boron content of the crop, accordingly, reflect a basic effect of particle size on the rate of release.

Conclusions

In essence, the data show that there exists for each glass composition a particular optimal particle diameter which will exhibit a higher degree of performance in single season use than any combination of differently sized particles. Below this optimal diameter much, if not all, of the advantage of using a glass carrier is lost, because the added boron dissolves too rapidly. Above this diameter, part of the added boron cannot be utilized in the initial season, because it remains in an undissolved condition. However, in the latter case, the benefit

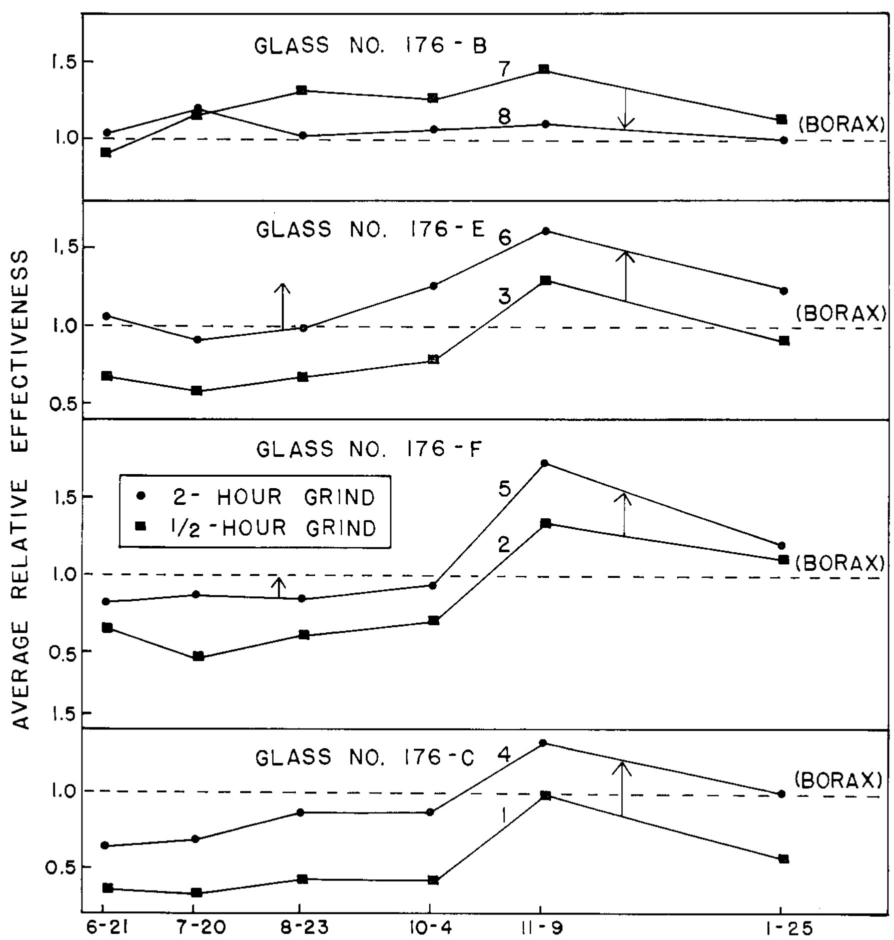

Figure 5. Relative effectiveness of grinds

Numbers on curves indicate order of increasing reactivity
Vertical arrows show direction of change with increasing fineness

to be derived from slow release may not be regarded as completely lost. The unsolubilized glass remaining in the soil will continue to release boron slowly for crops of subsequent seasons. On the basis of these considerations, the most suitable mill products were the 2-hour grind of 176-C, and the 0.5-hour grinds of 176-E and -F. The average effectiveness of these materials relative to borax was 0.6 ± 0.1 in the first two harvests. Over-all performance of such glass carriers can be improved greatly by narrowing the particle size range.

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FERTILIZER CONTAMINANTS

Rate of Biuret Formation from Urea

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To determine the amount of biuret formed under conditions encountered in the manufacture and transportation of urea, a kinetic study of the available data has been made. The rate constants of biuret formation from urea at different temperatures were determined and the results of calculations on biuret formation in urea solutions under various conditions are presented.

One of the main by-products obtained on heating urea, either in solid form or in aqueous solution, is biuret. However, the exact mechanism of biuret formation is not fully known and the literature on the kinetics of biuret formation is extremely limited (*1–7*).

A considerable amount of urea is used as fertilizer, in which the presence of biuret has to be controlled, because of its detrimental action on plants and leaves. It is therefore desirable to be able to estimate the rate of biuret formation from urea under various conditions. The results of a kinetic study, utilizing available data in biuret formation from urea are presented here. A weighed urea solution was heated at the desired temperature in a sealed glass test tube without stirring. It is believed that the data are valid for the usual conditions encountered in the production and transportation of urea.

Kinetic Study

At high temperatures, urea undergoes complex reactions to produce a mixture of several compounds, including triuret and cyanuric acid. However, under usual plant operating conditions for producing urea, the extent of formation of such compounds is relatively insignificant, as compared to the amount of biuret formation. Moreover, at the temperatures generally encountered in the transportation of urea, the formation of such compounds as well as the dissociation of urea into ammonia and carbon dioxide is relatively insignificant.

Therefore, the rate constants presented herein have been developed without consideration of the amounts of substances formed other than biuret as shown by the following equation:

$$2NH_2\text{—}CO\text{—}NH_2 \rightarrow NH_3 + NH_2\text{—}CO\text{—}NH\text{—}CO\text{—}NH_2$$

Then

$$\frac{d}{dt}(NH_2\text{—}CO\text{—}NH\text{—}CO\text{—}NH_2) = \frac{d}{dt}(NH_3) = \frac{-d}{dt}(NH_2\text{—}CO\text{—}NH_2)^2$$

$$\frac{dx}{dt} = k\,(a - x)^2 \quad (1)$$

where

d/dt = change of concentration with respect to time
a = initial concentration of urea in the solution, moles per liter
x = number of moles of urea reacted in the interval time t
t = time in hours
k = rate constant of the formation of biuret

$$\frac{dx}{(a - x)^2} = kdt \quad (2)$$

$$\frac{1}{a - x} = kt + c \quad (3)$$

when $t = 0, x = 0$. Hence

$$c = \frac{1}{a} \quad (4)$$

Substituting Equation 4 into 3,

$$kt = \frac{x}{a(a - x)} \quad (5)$$

Assuming $P = \frac{x}{a}$, the fraction of urea converted to biuret, is then

$$kt = \frac{P}{a(1 - P)} \quad (6)$$

These kinetic equations were applied to the available data (*5*). The rate constant of the reaction at 140° C. was calculated and the results are shown in Table I, which verifies the validity of the treatment because the rate constant remains substantially the same. The rate constants at different temperatures were determined in a similar manner and are reported in Table II.

Activation Energy

From Table II, when the logarithm of the rate constant is plotted against the reciprocal temperature (1/°K.), it is possible, by the Arrhenius equation, to obtain the energy of activation of biuret formation from urea at the temperature range of 50° to 170° C. Such an Arrhenius plot gives an essentially straight line, from which the activation energy is estimated as 20.3 kcal. per mole. By use of such rate constants the rate of biuret formation in urea solutions at different concentrations can be calculated for any temperature. Although biuret is formed at almost constant rate even at high temperatures, a progressive decrease occurs with time at the high temperature levels due to the slow condensation of biuret to triuret. However, the decrease is so slight that for practical purposes, it can be ignored. Thus,