

Corrosion of Metals by Liquid Mixed Fertilizers

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The corrosive effect of liquid mixed fertilizers on mild steel, stainless steel, and aluminum alloys was determined. Both mild steel and stainless steel were satisfactorily resistant with practically all combinations of variables tested. Aluminum resistivity ranged from unsatisfactory to satisfactory; conditions which had a significantly adverse effect were high phosphate content, high temperature, and aeration of sample. Beneficial conditions were presence of potash and use of inhibitor. There were some differences in resistivity of the aluminum alloys, but the effects of solution variables were much more important.

PRODUCTION OF LIQUID FERTILIZERS containing more than one plant nutrient is a rapidly growing industry (7, 8). Single nutrient liquids, such as anhydrous ammonia and nitrogen solutions, have been used in direct application to the soil for some time, but liquid mixtures is a relatively new field.

One of the problems facing the new industry is that of corrosion of tanks and equipment. For the manufacturing plant proper, the choice of construction material is between mild and stainless steel. Some plants have been built entirely of the latter, but the majority use mild steel for everything except the reactor vessel, which is normally built of stainless because raw acid may be present at one stage of the neutralization process. Even here, however, the trend has been toward reducing the amount of stainless used. Some plants now have mild steel reactors fitted with a small stainless steel "pot" or open-ended tube located near the center of the main tank. Ammonia and acid are reacted in the stainless steel vessel and overflow into the larger one. As the acid is neutralized by the time it contacts the mild steel tank wall, corrosion is minimized.

As far as is known, no test data were available on the resistance of mild steel when present plants were built. The choice presumably was dictated by economic considerations. However, some of the plants have now been in operation for 4 years or more and appear to be holding up well.

A more difficult problem is in regard to the use of aluminum tanks and application equipment. This metal is less resistant to liquid mixes and costs more. Therefore, mild steel is used when such mixes alone are handled. However, distributors and users of nitrogen solutions use aluminum equipment because it is much more resistant to such solutions than is mild steel. When dis-

tributors take on the additional venture of making or distributing liquid mixes and farmers start using them, corrosion becomes a problem because of the need to handle the new product in the existing aluminum equipment.

The only available data on the use of aluminum for liquid mixed fertilizers were reported recently by Vreeland and Kalin (10), who tested aluminum, mild steel, and stainless steel in various liquid mixtures. Stainless steel was not measurably affected but mild steel and aluminum were attacked; hence, Vreeland and Kalin suggested use of stainless steel for liquid mixed fertilizer equipment. However, the use of mild steel and aluminum is so firmly entrenched in industry practice that it is desirable to know what degree of corrosion will be found at varying levels of such factors as solution composition, temperature, aeration, welding, use of inhibitor, and type of alloy.

Measurements

Test Procedure. The submerged immersion type of corrosion test was used (9). Most of the tests were carried out in a thermal block test apparatus (Figure 1) and conformed in general to the procedure given in ASTM Designation A-224-46. Disk-type specimens $\frac{3}{4}$ to 2 inches in diameter and $\frac{1}{16}$ to $\frac{1}{4}$ inch thick, each having a hole $\frac{23}{64}$ inch in diameter at its center, were used. Welded specimens were prepared by cutting the disks in half, beveling the cut edges, and welding the halves together. The specimens were cleaned with acetone or toluene and air-dried.

The specimens were hung on glass lift rods centered in the test tubes and extended nearly to the bottom. The action of cams lifted and lowered the specimens through a distance of 1 inch, 19 times per minute. Thus, the average linear velocity of the specimens through

the test solution was 3.16 feet per minute. Cold water flowed through a condenser in the top of each tube to prevent excessive loss of water from the solution. When aeration of the solution was desired, hollow lift rods were used and air was passed through them at the desired rate. Temperature of the solution was controlled to within 3° F. of the desired value in tests at elevated temperatures; in those conducted at ambient temperature, the test temperature varied with the season, approximately between 30° and 100° F. Equipment limitations prevented closer control in the latter tests. The mean temperature during the test period is the test temperature.

At the end of the 28-day test period, the specimens were removed and scrubbed with a soft wire brush to remove corrosion products, after which they were dried and weighed to determine weight loss.

Tests carried out at 200° F. were made in a bomb to prevent loss of ammonia. Several specimens were mounted in the bomb with glass spacers between them and sufficient solution to submerge the specimens was added. The sealed bomb was submerged in a constant temperature bath and oscillated with a cam mechanism. The cam turned 19 revolutions per minute and lifted and lowered one end of the bomb through a distance of 2 inches. The specimens were handled the same as for the thermal block apparatus.

Materials. The metals tested included mild steel, stainless steel, and various aluminum alloys. All the materials were from regular mill products and were representative of commercially available materials. Typical steel compositions are given in Table I.

The aluminum alloys were chosen from the types currently used in storing and applying nitrogen solutions as well as those likely to be used for this purpose in the future. Magnesium alloys

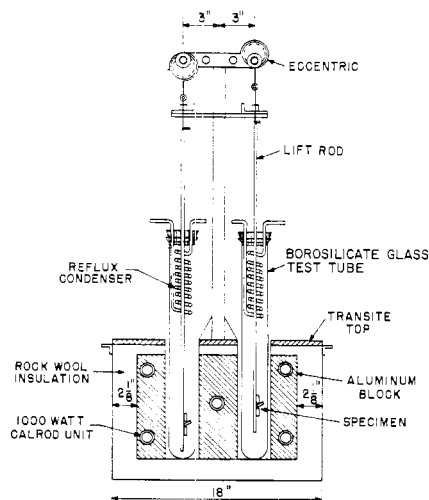


Figure 1. Section through thermal block, corrosion-testing apparatus

such as 5052 and 5154 are widely used in tank construction and 6061 in making piping. High-copper types such as 2011 are used in making parts on screw machines and a high-silicon type such as 4043 in making castings. In addition, wrought aluminum (1100), a manganese alloy (3003), and a high-magnesium, low-copper alloy were included. These are used in various ways and are noted for corrosion resistance. Typical compositions of the aluminum alloys are given in Table II.

The liquid mixed fertilizer test solutions were prepared from reagent grade salts and deionized water. The salts used were monoammonium phosphate, diammonium phosphate, ammonium nitrate, urea, and potassium chloride.

Design of Experiments and Interpretation of Data. Because of the large

number of variables which possibly could affect corrosion rate, the tests were set up in a statistical design. By this means, identification of significance could be made with a minimum number of tests and any interactions between variables could be identified. The factorial type of design was used, and in many cases "partial factorials" were employed when it was believed that the additional information which could be obtained from a complete factorial was not worth the time and cost of the additional tests.

High-order interactions are normally considered to be the result of experimental error rather than an actual relation between variables; therefore, such interactions were used in calculating the experimental error. In addition, preliminary tests showed that several of the variables had no significant effect on corrosion rate. As these tests were in effect duplicates, they were also used in computing the error. The standard deviation was estimated by these means to be about 25% of the corrosion rate, which agrees with results from previous work in which the same method of testing was used.

As the corrosion rate approaches a limiting value (zero), a logarithmic rather than an arithmetic basis was used in comparing results. The simple interactions were identified and quantitative expressions were derived for the combined effect of variables on corrosion rate for those metals which were most susceptible to corrosion.

Corrosion of Aluminum Alloys

In tests on aluminum, the alloys listed in Table II were tested with fertilizer

solutions having plant nutrient ratios of 1:1:1, 1:1:0, 1:3:1, and 1:3:0 (Table III). The experimental design included eight factors, discussed below, which might have an effect on corrosion rate. The conclusion as to significance in each case is based on a 95% confidence level.

Degree of Ammoniation. In practice, practically all liquid mix producers react enough ammonia with the phosphoric acid to give an ammonia to phosphoric acid mole ratio of about 1.69 (8). This corresponds to a 1 to 3 nitrogen to phosphorus pentoxide weight ratio and is a good compromise between loss of ammonia at higher ammoniation rates and increase in raw material cost if less of the relatively cheap ammonia is used. However, the 1.69 ratio is not the best for solubility, which is highest for many grades at a ratio of about 1.55. As in some areas salting-out temperature is of primary importance, degree of ammoniation was included as a test variable to determine the effect on corrosion rate. Reducing the ammonia to acid ratio lowers the pH somewhat (Table IV). However, no significant effect on corrosion rate was noted for degree of ammoniation in the 1.69 to 1.55 range.

Phosphate-Nitrogen Ratio. The phosphate content of the solutions was one of the most significant factors studied. The high-phosphate types (phosphorus pentoxide to nitrogen weight ratio = 3) were considerably more corrosive than the low-phosphate types (phosphorus pentoxide to nitrogen = 1). The mean increase in corrosion rate between the high and low levels was 3.3-fold. This effect was independent of other variables except welding, alloy type, and potassium oxide to nitrogen ratio.

There was a major interaction with the potash content, the adverse effect of high phosphate being much in potash-containing solutions. Similarly, the high phosphate intensified corrosion to a greater degree with alloy 3003 than with other alloys. The high-magnesium alloy was least affected by

Table I. Composition of Steels Used in Corrosion Tests

Type	Composition, % ^a							
	C	Mn	P	S	Ni	Cr	Mo	Si
Mild steel (AISI)								
C1042)	0.4-0.47	0.6-0.9	0.04	0.05
316	0.1	2.0	0.04	0.03	10.0-14.0	16.0-18.0	2.0-3.0	1.0
430	0.12	1.0	0.04	0.03	14.0-18.0	...	1.0

^a Composition in per cent maximum unless shown as a range.

Table II. Composition of Aluminum Alloys Used in Corrosion Tests^a

Type	Composition, %								
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others
1100-H14	(1.00) ^b		0.20	0.05			0.10		0.15
2011-T3	0.40	0.70	5-6				0.30		0.15
3003-H14	0.60	0.70	0.20	1-1.5			0.10		0.15
4043 ^c	4.5-6.0	0.80	0.30	0.05	0.05		0.10	0.20	0.15
5052-H32	(0.45) ^b		0.10	0.10	2.2-2.8	0.15-0.35	0.20		0.15
5154-H32	(0.45) ^b		0.10	0.10	3.1-3.9	0.15-0.35	0.20	0.20	0.15
6061-T6	0.40-0.80	0.70	0.15-0.40	0.15	0.8-1.2	0.15-0.35	0.25	0.15	0.15
High-Mg ^d alloy	0.20	0.20	0.05	0.10-0.20	6.5-7.5		0.00	0.10-0.25	Low

^a Composition in per cent maximum unless shown as a range (5). ^b Si + Fe.

^c Casting alloy. Specimens were castings made for use as nozzle clamps. ^d Sources of chemical analysis (4).

Table III. Corrosion of Aluminum Alloys in Liquid Fertilizers

Alloy	Temp., ° F.	Test Conditions ^a	Corrosion Rate, Mils Penetration/Yr.				
			8-8-8	10-10-10	12-12-0	6-18-6	8-24-0
1100-H14	64	A, C, G	5.2		32.8		
	64	A, D, G		7.0	38.0 ^b		
	64	B, C, G	6.7				
	64	B, D, G		6.7			
	72	B, C	5.0				48.4
	72	B, C, E			0.4	1.2	1.3
	80	A, C	6.5				
	80	A, D		5.6			
	80	B, C	12.1				83.5
	80	B, D		10.5			
	122	B, C			120.3	42.8	
	122	B, C, E	5.2				39.7 ^c
2011-T3	72	B, C	6.2		35.3	16.5	61.8
	72	B, E					39.6
	80	B, C, G	5.9				
3003-H14	44	B, C	1.6				24.2
	44	B, C, E			1.4	1.9	
	44	B, C, F			29.7	14.7	
	44	B, C, G			12.9	13.2	
	44	B, C, E, F	1.0				7.4
	44	B, C, E, G	1.4				3.1
	44	B, C, F, G	6.7				25.9
	44	B, C, E, F, G			2.3	1.4	
	72	B, C			32.2	18.5	
	72	B, C, E	0.4				7.7
	72	B, D			34.4		
	72	B, D, E	1.2				
	122	B, C	14.6				280.5
	122	B, C, E			4.2	5.6	
4043	80	B, C	9.2		76.1	22.5	86.8
5052-H32	72	B, C	7.0		38.7	16.8	99.6
	72	B, C			31.1	18.9	
	72	B, C, E	0.1				3.2
	80	B, C, G	7.0				
	122	B, C	9.1				353
5154-H32	72	B, C	9.0		40.4	16.3	104.4
	72	B, E					3.4
	80	B, C, G	8.9				
6061-T6	72	B, C	6.6 ^d		34.2	29.0	101.8
	72	B, E					8.2
	80	B, C, G	4.5				
High-Mg alloy	72	B, C			26.1	14.7	
	72	B, C, E	1.1				5.0
	122	B, C	6.3				136
	122	B, C, E			21.2	15.9	

^a A, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.55$.B, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.69$.

C, supplemental nitrogen (if any) supplied as ammonium nitrate.

D, supplemental nitrogen (if any) supplied as urea.

E, inhibitor (0.1% $\text{Na}_2\text{Cr}_2\text{O}_7$) added to solution.

F, solution aerated at the rate of 0.02 cubic foot per minute.

G, specimen welded by the acetylene welding process with welding rod containing 94.0 to 94.5% aluminum and having silicon as the major impurity.

^b Localized attack on weld.^c Uninhibited 8-24-0 at 175° F. gave a rate of >1600 mils per year. Sample was completely destroyed.^d Pitted at rate equivalent to 117 mils penetration per year.

Table IV. pH of Liquid Mixed Fertilizers

Grade	$\text{NH}_3/\text{H}_3\text{PO}_4$ Mole Ratio	Source of Supplemental Nitrogen	pH
12-12-0	1.69	NH_4NO_3	6.3
	1.69	Urea	7.0
	1.55	NH_4NO_3	5.9
	1.55	Urea	6.6
8-8-8	1.69	NH_4NO_3	6.5
10-10-10	1.69	Urea	7.0
8-8-8	1.55	NH_4NO_3	6.0
10-10-10	1.55	Urea	6.5
6-18-6	1.69	...	6.4
8-24-0	1.69	...	6.4

procedure. The aluminum corrosion products were identified as ammonium-alumino phosphates with part of the ammonium replaced by potassium in the product from potash-containing solutions. Possibly the presence of the potassium in the crystal lattice makes the compound adhere more closely to aluminum. However, sufficient data to establish this were not obtained.

Urea vs. Ammonium Nitrate. Liquid mixtures having a nitrogen to phosphorus pentoxide weight ratio higher than 1 to 3 require a supplementary source of nitrogen in addition to the ammonia used in neutralizing phosphoric acid. The majority of producers use urea rather than ammonium nitrate because higher solubility is obtained. However, some use ammonium nitrate and there is a growing trend toward urea-ammonium nitrate solution. The relative contribution of the two materials to corrosion was one of the variables considered in this study.

There was no significant difference between corrosion rates in solutions containing urea and those containing ammonium nitrate. As shown in Table IV, substitution of urea for ammonium nitrate increased the pH by half a unit or more. However, this was not sufficient to affect corrosion significantly.

Use of Inhibitor. Inhibitors are widely used for protecting aluminum alloys. For example, strong calcium chloride brines are successfully handled by using sodium dichromate as an inhibitor (2). The mechanism involved is polarization of anodic areas (3).

Addition of 0.1% sodium dichromate to the solutions decreased corrosion in most instances by about 90%. There were slight differences in effect between potash-containing and nonpotash solutions, and considerable differences among alloys and between temperatures. At 72° F. the corrosion rate was reduced 94% by the inhibitor; at 122° F. the reduction was 84%. Alloy 5052 was particularly well protected by the inhibitor while the high-magnesium alloy and 2011 alloy were least protected. The inhibitor was not very effective for 2011 alloy in 8-24-0.

the phosphate to nitrogen ratio. High phosphate content as a rule had the most adverse effect when the other variable was at its most beneficial level.

Potash-Nitrogen Ratio. One of the more surprising results of the study was the beneficial effect of potash. Corrosion was expected to increase because the potash is associated with chloride, one of the most corrosive agents to aluminum. However, the presence of potash (potassium oxide to nitrogen = 1) reduced corrosion by as much as 83% as compared to nonpotash solutions. There were interactions with phosphorus pentoxide to nitrogen ratio (as

discussed above), presence of inhibitor, and welding.

The beneficial effect of potash and a low phosphate nitrogen ratio is shown in Figure 2.

The mechanism of the protection by potash is not clear. Samples exposed to potash-containing solutions developed a thin, white coating whereas those in nonpotash solutions did not. The latter often produced a white corrosion product but it was dispersed in the solution rather than attached to the alloy surface. The adherent coating produced by the potash solutions was removed easily by the washing involved in the weighing

As the sodium dichromate was effective, other commonly used inhibitors—such as other chromates, gelatin, or sodium silicate—were not tested. Possibly a lower concentration of the dichromate would be adequate, but this was not investigated. Another consideration is that a lower chromate level might be desirable to avoid possible toxicity to plants (6).

Welding. The effect of welding on corrosion was studied in 20 tests. Although there was no independent significance, the effect in relation to other variables was significant. Welding had an adverse effect at the most beneficial level of variables such as phosphorus pentoxide to nitrogen ratio, potassium oxide to nitrogen ratio, and aeration; at the most adverse level of these variables, however, welding had a small beneficial effect. Pitting of welded areas was rare; however, it occurred more frequently in inhibited than in noninhibited solutions.

Aeration. Tests on the effect of aeration were all made with alloy 3003. A mean increase in corrosion rate of 2.4-fold was obtained with nonwelded specimens but the effect on welded ones was not significant.

Type of Alloy. Of the eight alloys tested, no one alloy was markedly superior or inferior to the other alloys under all conditions. Certain alloys, however, were either resistant or susceptible to attack for specific conditions. Alloy 1100 was the most resistant alloy at room temperature, while alloy 3003 gave the best results at the high temperature (122° F.). The high-magnesium alloy was superior to the other alloys in uninhibited solutions. Alloy 5052 corroded least of all alloys in the presence of inhibitor or in potash-containing solutions, but it did not withstand high-phosphate, nonpotash solutions very well. Alloy 5154 appeared to parallel the behavior of alloy 5052 at room temperature. Alloys 2011 and 6061 likewise corroded similarly to alloy 5052 at room temperature with some exceptions. Alloy 2011 was relatively resistant to 8-24-0, but adding inhibitor to this solution was rather ineffective. Alloy 6061 was corroded somewhat more in 6-18-6 than were the other alloys. Alloy 4043 casting was attacked relatively severely by 12-12-0.

Corrosion of aluminum by neutral solutions normally takes the form of pitting rather than general surface attack (2). Under the conditions of this study, however, no pitting was observed on any of the unwelded samples exposed at room temperature except for 6061. In 8-8-8 solution, this alloy was pitted severely, to a depth equivalent to 117 mils penetration per year. This was not observed in tests of 6061 with other solutions.

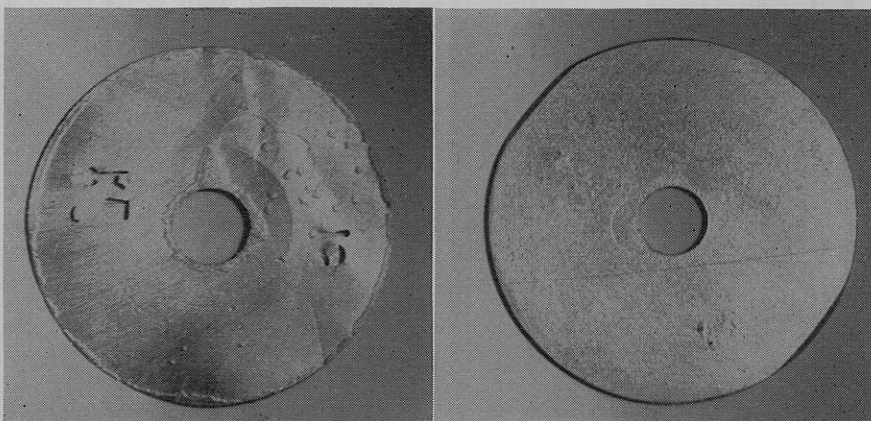


Figure 2. Protective effect of potash and low phosphate-nitrogen ratio

Left. Aluminum alloy 3003 exposed to 8-24-0 solution at 122° F. Sample almost destroyed; corrosion rate was 280.5 mils per year. Right. Same alloy exposed to 8-8-8 solution at 122° F. Corrosion rate was only 14.6 mils per year

Effect of Temperature. Most of the tests in this study were run at ambient temperature (mean temperature of 44° to 80° F.). However, in practice higher temperatures would be encountered at times, either from handling uncooled solutions from the neutralizing tank or because of heating of tanks and application equipment by the sun. For this reason a set of tests was made at 122° F. Corrosion was considerably more severe at the higher temperature. Ratios of the rates at 122° and 72° F. were 10.1, 2.7, 5.0, and 3.4 for alloys 1100, 3003, 5052, and the high-magnesium alloy, respectively. The effect was independent of the phosphorus pentoxide to nitrogen ratio but there were significant interactions with both the potassium oxide to nitrogen ratio and the presence of inhibitor. The latter interaction was highly significant in that the temperature effect was 2.7-fold in uninhibited solutions compared to an 8.0-fold increase in inhibited solutions.

Typical surface conditions of specimens tested at 122° F. are shown in Figure 3.

Pitting was observed on the specimens tested at high temperature in inhibited 6-18-6 and 8-24-0 solutions, the latter being especially severe. Apparently the amount of inhibitor was not sufficient to fully protect against the high phosphate content and pitting therefore was promoted. This is a common effect in use of inhibitors with aluminum (2).

Nature of Corrosion Products. Many of the samples contained a suspension of white corrosion product after the exposure period. At high corrosion rates, the precipitate was large and voluminous. Microscopic examination showed two phases present—monoammonium phosphate and an unidentifiable insoluble phase. The two phases were separated by filtering, repulping, and refiltering several times, and washing with acetone. Chemical analyses of the insoluble products are shown in Table V.

The analyses indicated that the insoluble products were hydrated ammonium-aluminum phosphates or ammonium-potassium-aluminum phosphates, appearing as single crystalline phases. The x-ray diffraction pattern of compound I was distinctly different from those of compounds II and III; the latter two materials had similar x-ray patterns, perhaps because of isomorphous substitution of potassium ion for ammonium ion in the crystal lattice. The product compositions correspond fairly well with the postulated formulas. The probable exchange of the univalent cations—ammonium, potassium, and hydrogen—from the media with the corrosion products precludes any absolute identification of the formulas. Presumably a series of compositions is possible of the general formula $[(NH_4)_a(K)_b(H)_c]_{n-m}Al_m(PO_4)_n \cdot xH_2O$ where $a + b + c = 3$, and n , m , and x are integers. The x-ray pattern changes, perhaps, only with n , m , and x .

Quantitative Correlation of Variables. An equation was developed which expresses the corrosion rate in terms of three of the main variables:

$$\log y = a + b(P_2O_5:N) + c(K_2O:N) + dT + e(K_2O:N)(T) \quad (1)$$

where y is mils penetration per year, T is ° F., and $P_2O_5:N$ and $K_2O:N$ are weight ratios. The equation applies only to the ranges studied—i.e., $P_2O_5:N = 1$ to 3, $K_2O:N = 0$ to 1, and $T = 72^\circ$ to 122° F. As there were interactions also with type of alloy and presence or absence of inhibitor, the parameters of Equation 1 varied with these factors. Values for different combinations are given in Table VI for four alloys—1100, 3003, 5052, and the high-magnesium alloy. The use of Equation 1 to predict the corrosion rates of the other alloys is not warranted inasmuch as their temperature effects and interactions were not determined.

Values calculated from Equation 1 for several fertilizer grades and alloys are given in Table VII. Observed values

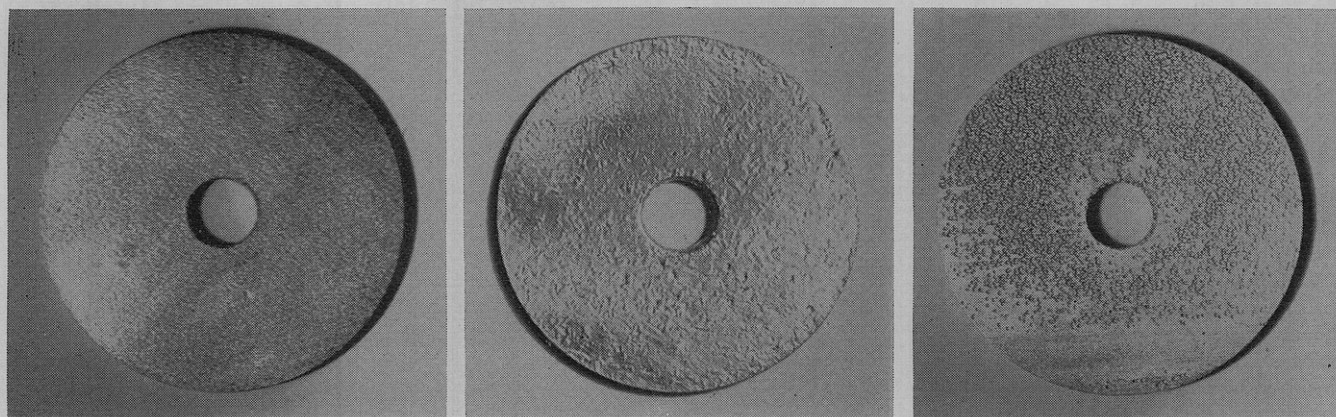


Figure 3. Corrosion of wrought aluminum at 122° F.

Left. Medium attack (42.8 mils per year) by 6-18-6 solution

Center. Heavy attack (120.3 mils per year) by 12-12-0

Right. Pitting attack by 8-24-0 containing inhibitor, with over-all corrosion at 39.7 mils per year

show the degree to which the equation fits the experimental data. For the combinations not tested in the present study the following assumptions are made: The effects of the variables phosphorus pentoxide to nitrogen, potassium oxide to nitrogen, and temperature are continuous and linear over their respective ranges. The interactions between variables for a particular alloy remain constant over the ranges of the variables—i.e., there are no significant interactions of third order or higher.

Equation 1 was tested against data reported by Vreeland and Kalin (10) for alloy 3003. Their test conditions required some extrapolation in temperature and solution composition and their results, reported in terms of total specimen surface, were recalculated on the basis of submerged surface, which was only two thirds of the specimen area. This seems reasonable as most of the attack on aluminum samples occurred in the liquid zone. The results of the comparison are given in Table VIII. Agreement is very good for 8-24-0 and order of magnitude agreement is obtained for the other solutions. The greatest discrepancy is with 3-9-9, which involved extrapolation from the potassium oxide to nitrogen ratio of 1 to 1 in the present study to 3 to 1. It is not surprising that this extrapolation did not give good agreement, as it would hardly be expected that the second and third increments of potash would affect corrosion to the same degree as the first.

Evaluation. Aluminum appears to be in a marginal category in regard to usability with liquid mixed fertilizers. Between the extremes of clearly acceptable and unacceptable results, several combinations of conditions gave corrosion rates which may or may not be acceptable, depending on factors such as type of equipment, uniformity of corrosion over the metal surface, and the many economic factors which enter into the determination of acceptable life of equipment. Several arbitrary

Table V. Properties of Insoluble Aluminum Corrosion Products

Alloy	Fertilizer Grade	Product Composition, %				Compound ^a
		N	P ₂ O ₅	Al ₂ O ₃	K ₂ O	
3003 ^b	12-12-0	9.7	52.7	24.6	..	I
	8-24-0	8.5	43.5	15.2	..	II
	8-8-8	4.4	40.9	14.6	12.6	III
	6-18-6	3.6	40.4	16.1	12.6	III
5052 ^c	12-12-0	8.5	43.5	15.6	..	II
	8-24-0	8.5	43.7	15.7	..	II
	8-8-8	4.2	40.3	15.4	11.8	III
	6-18-6	4.5	40.9	14.6	12.8	III

^a Corresponds approximately to following formulas:

	%			
	N	P ₂ O ₅	Al ₂ O ₃	K ₂ O
I = (NH ₄) ₃ Al ₂ (PO ₄) ₃ ·H ₂ O	10.2	51.7	24.8	0.0
II = (NH ₄) ₂ HA(PO ₄) ₂ ·4H ₂ O	8.6	43.6	15.6	0.0
III = NH ₄ KHA(PO ₄) ₂ ·4H ₂ O	4.0	40.9	14.7	13.6

^b Temperature, 122° F.

^c Temperature, 72° F.

classification schemes are available in the literature but they vary widely in the values specified for the various ratings. Most of them, however, list a value between 20 and 60 mils per year as the upper limit of the good, satisfactory, or acceptable range. On this basis, the following ratings are used in this paper:

Fully acceptable	<20 mils per year
Possibly acceptable	20-60 mils per year
Not acceptable	>60 mils per year

Even this is only an arbitrary and general classification. Laboratory tests can give only a general indication of what may occur in practice, where varying corrosion environments may exist in various steps of a single process.

On the above basis, acceptable rates were obtained for all alloys in potash-containing solutions at room temperature; however, acceptability varied under other combinations of conditions (Table VII).

Although some of the combinations can be rated as acceptable, this applies only to situations in which the surface attack is fairly uniform—as was found in most of the tests. However, pitting of 6061 at room temperature was ob-

served and some welded samples pitted on the welded area. Vreeland and Kalin (10) also found some pitting attack on unwelded samples in the vapor zone at elevated temperature. Pitting of aluminum is reported to be a matter of probability rather than a specific defect (7); pitting sites are thought to arise in random fashion through the interaction of numerous anodic and cathodic areas on the metal surface. Extended use tests probably would be required to fully evaluate the effect of pitting on usability.

Of the factors which can be varied to favor use of aluminum, use of an inhibitor is one of the most effective. With inhibitor, practically all the combinations of conditions receive a fully acceptable rating. The principal exception is 8-24-0 at 122° F., which would be possibly acceptable. That some plants have coolers is another favorable factor, as the solution could be cooled to a generally noncorrosive level before storage or shipment. Time of exposure is an additional consideration, especially for transfer and application equipment. Such equipment may be used only a few months per year, so that if it were

Table VI. Values for Constants in Equation for Corrosion of Aluminum by Liquid Fertilizers

Constant	Alloy without Inhibitor				Alloy with Inhibitor			
	1100	3003	5052	High Mg alloy	1100	3003	5052	High Mg alloy
a	-0.0664	0.3816	0.5079	0.6808	-2.3415	-0.6968	-2.1496	-1.4411
b	0.2604	0.2718	0.2767	0.2022	0.2604	0.2718	0.2767	0.2022
c	-0.2075	-0.9217	-0.4201	-0.1530	0.1265	-0.9217	-0.2537	0.3046
d	0.01475	0.00956	0.01078	0.00726	0.02594	0.00956	0.02389	0.02098
e	-0.00531	0.00367	-0.00677	-0.00688	-0.00531	0.00367	-0.00677	-0.00688

Table VII. Some Calculated and Observed Corrosion Rates for Aluminum Alloys in Liquid Fertilizers^a

Grade of Fertilizer	Temp., ° F.	Inhibitor ^b	Corrosion Rate, Mils Penetration per Yr.			
			1100	3003	5052	High Mg alloy
12-12-0	72	No	18.0	22.0 (32.2)	36.3 (34.9)	25.5 (26.1)
	72	Yes	0.6 (0.4)	1.8	0.7	1.9
	122	No	98.6 (120.3)	66.1	125	58.7
	122	Yes	12.1	5.5 (4.2)	11.0 (12.9)	20.9 (21.2)
8-24-0	72	No	59.8 (48.4)	76.8	130 (99.6)	64.6
	72	Yes	2.0 (1.3)	6.4 (7.7)	2.5 (3.2)	4.7 (5.0)
	122	No	327	231 (280)	448 (353)	149 (136)
	122	Yes	40.3 (39.7)	19.3	39.3	53.1
8-8-8	72	No	4.6 (5.0)	4.8	4.5 (7.0)	5.7
	72	Yes	0.3	0.4 (0.4)	0.1 (0.1)	1.2 (1.1)
	122	No	13.7	22.2 (14.6)	7.2 (9.1)	6.0 (6.3)
	122	Yes	3.7 (5.2)	1.9	0.9	6.1
6-18-6	72	No	15.4	16.9 (18.5)	16.1 (17.6)	14.5 (14.7)
	72	Yes	1.1 (1.2)	1.4	0.5	3.1
	122	No	45.6 (42.8)	77.6	25.6	15.2
	122	Yes	12.1	6.5 (5.6)	3.2 (2.8)	15.5 (15.9)
9-18-0	72	No	32.8	41.1	68.6	40.5
	122	No	180	124	237	93.5
7-14-7	72	No	8.5	9.1	8.5	9.1
	122	No	25.0	41.5	13.5	9.5
8-16-4	72	No	16.7	19.3	24.2	19.2
	122	No	67.1	71.7	56.8	29.8
10-10-5	72	No	9.1	10.3	12.8	12.1
	122	No	36.8	38.3	30.0	18.7
8-24-4	72	No	30.3	36.1	45.8	30.6
	122	No	122	134	107	47.5

^a Quantities in parentheses indicate observed corrosion rates. ^b 0.1% Na₂Cr₂O₇.

Table VIII. Comparison of Test Data for 3003 Alloy

Solution ^a	Corrosion Rate, Mils Penetration per Yr.	
	Vreeland and Kalin (10) ^b	Present study ^c
6-6-6	21.3	33.0
10-10-5	38.9	54.1
8-24-0	300.6	308
3-9-9	37.1	16.2

^a Supplemental nitrogen from ammonium nitrate. Solution temperature, 135° F.

^b Computed on basis of submerged area.

^c Calculated from Equation 1.

washed out well after use the life would be extended and a nonacceptable or dubious rating thereby changed to an acceptable one. The same consideration would apply to storage tanks if they were emptied and washed at the end of the busy season.

The above precautions are most necessary with low-potash, high-phosphate solutions. To the extent that these can be avoided, the situation would be improved. Thus the corrosion prob-

lem will vary between areas because of differences in grades used.

Corrosion of Mild Steel

Tests at Room Temperature. Use of mild steel for storing and handling liquid mixtures is apparently satisfactory (7). However, as no data on corrosion at ambient temperature are available, some tests were included in the present study (Table IX). Variables were included as in the test on aluminum.

All the variable combinations tested gave values well within the fully acceptable range. The corrosion rates were so low that any effect of variables had little practical significance. The only one that gave an appreciable increase in corrosion was high phosphorus pentoxide to nitrogen ratio.

Although rates were very low, specimens exposed to potash-containing solutions rusted quickly on subsequent exposure to air (Figure 4). A series of tests was made to determine the extent of corrosion which might result from this cause in filling and emptying tanks in practice as well as from tanks and

equipment standing empty for extended periods. The standard 28-day test was used but the specimens were alternately immersed in the solution and suspended in air. During the first 14 days the immersion period was 8 hours followed by suspension in air for 16 hours; during the last 14 days this was reversed. Thus the specimens were suspended in air for one half the time. After completion of the 28-day test the specimens were exposed to air for 6 months and the weight loss determined (Table X).

Again all combinations of variables gave values well within the fully resistant range. Corrosion on further exposure to air was negligible. In the initial tests, the use of inhibitor had the most significant effect of any of the variables, reducing the corrosion rate by about 90% (mean value). However, the level of corrosion is so low that use of inhibitor would hardly be warranted.

A solution of potassium chloride was included to test the effect of potash alone. The relatively high corrosion rate obtained indicates a strong chemical interaction between the potash and other constituents in mixtures, as addition of

potassium chloride to a nonpotash solution reduces corrosion significantly.

Tests at Elevated Temperature. One of the most corrosive services for mild steel is in use as a holding vessel in conjunction with a small stainless steel reactor mounted inside it. Acid and ammonia react in the stainless steel vessel and the hot neutral solution flows out into the mild steel tank. In such plants, the solution ordinarily is cooled by recycling through a cooler but the tank walls may be exposed at times to solution at a fairly high temperature. Moreover, there are instances of use of mild steel alone for the reactor. In normal plants, pipes, pumps, and tanks after the stainless steel reactor are exposed to elevated temperatures.

Results of tests made at 165° to 200° F. are given in Table XI. At the higher temperature, a somewhat greater degree of corrosion was encountered but all of the rates were either in the fully acceptable range or very close to it. The following variables had a significant effect:

The high-phosphate types (1-3-x) of liquid fertilizers were three times as corrosive as the low-phosphate types (1-1-x).

The potash-containing liquid fertilizers (1-x-1) were 60% as corrosive as the nonpotash types (1-x-0).

The addition of 0.1% sodium dichromate decreased the corrosion rate 95%.

Aeration at 0.02 cubic foot per minute increased the corrosion rate 100%.

The tests were not sufficient to identify interactions between variables.

Some of the specimens exposed to high-phosphate solutions and high temperature developed protective coatings similar to that produced by Parkerizing steel (Figure 5). The same effect, but more pronounced, was observed on the specimen exposed to 10-10-10 solution at 200° F. The effect appeared to be considerably reduced in solutions which were aerated or which contained inhibitor. Development of such a coating on equipment surfaces may give subse-

Table IX. Corrosion of Mild Steel by Liquid Mixed Fertilizer at Room Temperature^a

Test Conditions ^b	Corrosion Rate, Mils Penetration per Yr.				
	8-8-8	10-10-10	12-12-0	8-24-0	9.3-29.9-0
A, C	0.8		0.9		
A, D		0.6	0.8		
B, C	0.6		0.6	1.2	1.7
B, D		0.4	0.6		
B, G				1.1	2.1

^a Approximate range, 75° to 100° F. ^b A, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.55$. B, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.69$. C, supplemental nitrogen (if any) supplied as ammonium nitrate. D, supplemental nitrogen (if any) supplied as urea. G, welded.

Table X. Corrosion of Mild Steel at Room Temperature under Conditions of Alternate Submersion in Liquid Fertilizers and Suspension in Air

Grade		pH	Test Conditions ^a	Corrosion Rate, Mils Penetration per Yr.			
				Initial Tests		Further Exposure to Air for 6 Months	
				Without inhibitor	With inhibitor ^b	Without inhibitor	With inhibitor
8-8-8	5.9	A, C	0.8		0.02		
	6.1	B, C		0.9		0.02	
10-10-10	7.0	A, D	0.9	0.03	0.04	0.04	
	7.0	B, D					
6-6-12	5.8	A, C	0.7	0.4	0.03	0.05	
	6.2	B, C					
	6.2	A, D					
	6.6	B, D					
5-10-10	5.9	A, C	1.2		0.04		
	6.3	B, C		0.2		0.05	
6-12-12	6.8	A, D	0.8	0.1	0.03	0.05	
	6.7	B, D					
8-16-8	5.8	A, C	1.0	0.1	0.02	0.05	
	6.2	B, C					
	6.1	A, D					
	6.4	B, D					
0-0-16.8 ^c	7.2		25.5	0.1	0.006	0.04	

^a A mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.55$. B, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.69$. C, supplemental nitrogen supplied as ammonium nitrate. D, supplemental nitrogen supplied as urea.

^b 0.1% $\text{Na}_2\text{Cr}_2\text{O}_7$. ^c 26.5% KCl solution.

quent protection against solutions which do not form the coating. In view of the generally low level of corrosion of mild steel, however, this possibility was not investigated and the conditions affecting development of the coating were not investigated thoroughly.

Evaluation. Mild steel was either fully acceptable or very close to it under all combinations of variables tested and no serious pitting was observed on any of the specimens. However, Vreeland and Kalin (10) found severe pitting in the vapor zone of tanks containing liquid mixed fertilizer. These tests were carried out in closed tanks at 135° F. This

effect has not been reported by plant operators, possibly because temperature level averages lower in practice.

Corrosion of Stainless Steel

Industrial use of stainless steel in liquid mixed fertilizer reactors has shown it to have a high resistance to the reactants and the product solutions. Tests were made, however, to get quantitative data on the corrosion rate of temperatures near the boiling point such as are reached in stainless steel reactors. A few tests were also included at room temperature. Corrosion rates were very low and most were negligible (Table XII).

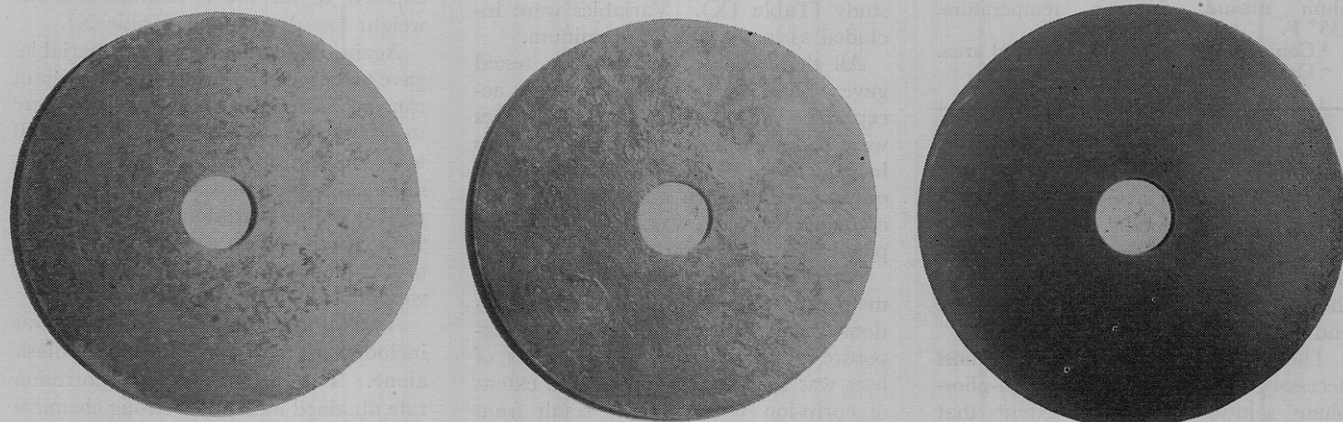


Figure 4. Rusting effect of potash on mild steel

Left. Medium rusting by 6-12-12 solution. Center. Heavy rusting by 0-0-16.8 (KCl solution). Right. No attack by 8-24-0 solution

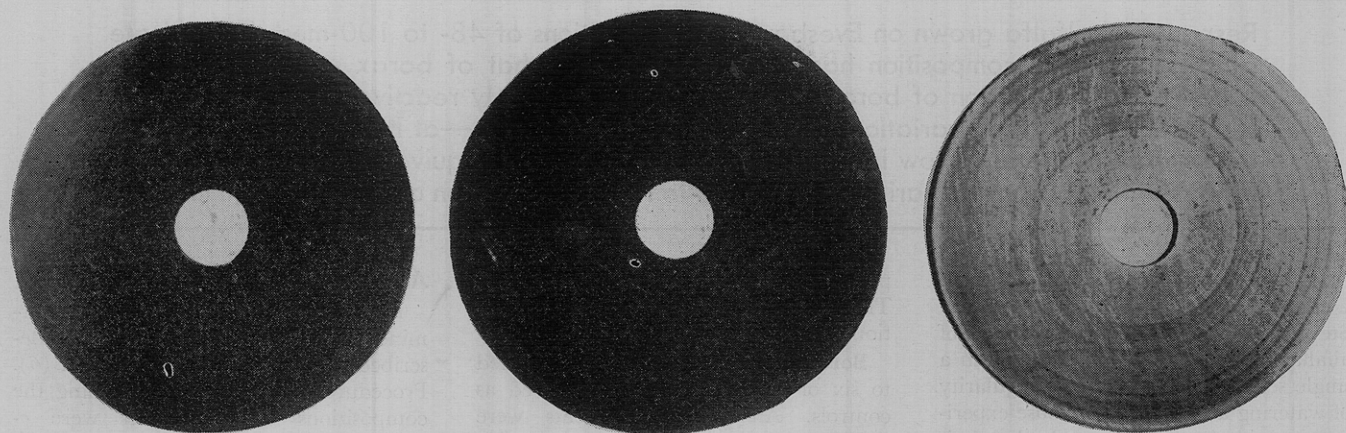


Figure 5. Parkerizing effect on mild steel

Left. Medium coating on specimen exposed to 9.3-29.9-0 solution at 175° F. Center. Heavy coating on specimen exposed to 10-10-10 at 200° F. Right. No coating on specimen exposed to 9.3-29.9-0 at room temperature

Table XI. Corrosion of Mild Steel by Liquid Mixed Fertilizer at Elevated Temperature

Grade	Test Conditions ^a	Temp., ° F.	Corrosion Rate, Mils Penetration per Yr.
8-8-8	B, C	165	1.6
	B, C, E	175	0.1
10-10-10	A, D	200	0.7
	A, D, G	200	0.7
12-12-0	B, C	175	2.1
	B, C, E	165	0.2
6-18-6	B	175	5.1
	B, E	165	0.3
8-24-0	B, E	175	0.2
	B, F	165	18.1
	B, G	175	7.7
	B, F, G	170	22.7
9.3-29.9-0	A	175	7.6
	A, G	175	8.4
	A, F	170	22.1

^a A, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.55$. B, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.69$. C, supplemental nitrogen (if any) supplied as ammonium nitrate. D, supplemental nitrogen (if any) supplied as urea. E, inhibitor (0.1% $\text{Na}_2\text{Cr}_2\text{O}_7$) added to solution. F, solution aerated at the rate of 0.02 cubic foot per minute. G, specimen welded.

Table XII. Corrosion of Stainless Steel by Liquid Mixed Fertilizer

Grade	Test Condition ^a	Temp., ° F.	Corrosion Rate, Mils Penetration per Yr.	
			Type 430	Type 316
8-8-8	A, C	Room	0.01	
10-10-10	A, D	Room	0.1	
	A, D	200	0.07	
	A, D, G	200	<0.01	0.01
	A, D, G ^b	200	1.3	0.7
9.3-29.9-0	A	175	0.02	
12-12-0	A, C	Room	0.9	

^a A, mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = 1.55$. C, supplemental nitrogen (if any) supplied as ammonium nitrate. D, supplemental nitrogen (if any) supplied as urea. G, specimen welded. ^b Specimen heat treated (after welding and machining) at 1950° F. for 9 minutes, then water-quenched. No further sanding or buffing of specimen was performed.

Literature Cited

- (1) Aziz, P. M., Godard, H. P., *J. Electrochem. Soc.* **102**, 577-9 (1955).
- (2) Eldredge, G. G., Mears, R. B., *Ind. Eng. Chem.* **37**, 736-40 (1945).
- (3) Evans, U. R., *Trans. Electrochem. Soc.* **69**, 213-31 (1936).
- (4) Jobbins, Wm. F., Inc., Aurora, Ill., Bull. 354.
- (5) *Materials & Methods* **43**, No. 1, 113 (1956).

- (6) Rediske, J. H., *U. S. Atomic Energy Comm.* **HW-42969** (May 7, 1956).
 - (7) Slack, A. V., *Com. Fertilizer* **95**, 28-9, 33, 35-7, 39-40 (August 1957).
 - (8) Slack, A. V., *J. Agr. Food Chem.* **3**, 568 (1955).
 - (9) Tennessee Valley Authority, Chem. Eng. Rept. No. 9 (1951).
 - (10) Vreeland, D. C., Kalin, S. H., *Corrosion* **12**, No. 11, 569t-75t (1956).
- Received for review November 1, 1957. Accepted April 12, 1958. Division of Fertilizer and Soil Chemistry, 132nd Meeting, ACS, New York, N. Y., September 1957.

GLASS AS A BORON SOURCE

Effect of Composition [and Reactivity of Borosilicate Glass on Boron Status of Alfalfa

A BORON CARRIER capable of moderately slow release of boron to a boron-deficient soil under crop stress is a recognized need. Ground borosilicate glass, obtained by quenching the melt in water and called frit in trade (9), is of special interest because its reactivity—i.e., the rate of nutrient release within soil—may be adjusted over a wide range by altering composition.

Exploratory vegetative tests in this laboratory and elsewhere (7) show that certain glasses will eliminate a boron deficiency condition of a soil. The influence of a slightly reactive glass persists. Boron content of alfalfa remains in the same range for 2 or more years. Furthermore, toxic levels are not reached in the crop even when the amounts of boron contained in glass applications are

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considerably above the upper limit for borax. These advantages have recently led to some commercial-scale use, but there still remains the problem of characterizing the influence of glasses with sufficient exactness to facilitate most effective utilization of their properties.

The variation in boron content of a crop as caused by seasonal differences in growth conditions greatly complicates