

Review of the Effects of Siliceous Dressings on the Nutrient Status of Soils

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A review of the literature on the effects of soluble silicates, basic slags, and silicophosphate fertilizers on plant growth shows that the value of soluble silicates lies solely in the ability of silicate ions to displace phosphate from soil colloids, thus enhancing its availability. Basic slags low in phosphorus act primarily as liming materials; there is no evidence that they have appreciable effect on the nutrient status of the soil. The fertilizing action of high-phosphorus basic slags is due to their phosphorus content; by comparison, their silicon content is of little importance.

UNDERLYING FACTORS in the response of crops to dressings of siliceous materials are best reviewed by grouping them into three classes: Colloidal silica and soluble silicates of potassium, sodium, calcium, and magnesium; calcium silicate slags containing less than 10% of phosphoric oxide that are by-products of blast and electric furnace processes; silicophosphate fertilizers and basic slags produced as by-products of the steel industry (about 30% of phosphoric oxide).

Soluble Silicates

An effect of soluble silicate on plant growth was observed as early as 1868, when applications of soluble silicates were included in the permanent barley experiment at Rothamsted. In analyzing data from this experiment in 1906, Hall and Morison (17) pointed out that the ratio of silicon to phosphorus in plant ash was increased markedly by silicate treatments. Their conclusion that concomitant increase in yield might have resulted from a more efficient use of phosphorus by plants containing large amounts of silicate was refuted by Fisher (13), whose review of the data in 1929 showed that increase in yield was due entirely to an increased availability of phosphorus in the soil and not to a change in plant metabolism. Fisher noted that an application of silicate always led to an increase in the phosphorus content of the dry plant, even on plots which had received no phosphate fertilizer for many years, and that decrease in percentage of phosphorus in the ash resulted from the large silica content. Fisher also observed a close correlation between the phosphorus content of plants and crop yield. When both silicate and phos-

phate were applied, however, the increase attributable to the silicate was much less than that from the phosphate fertilizer.

Fisher's conclusions agree with those of contemporary workers in Germany. When the supply of soluble phosphate in a soil was inadequate for satisfactory growth of rye, Lemmermann and Wiessmann (23) found that applications of soluble silicates stimulated growth, and Densch (10) obtained similar results with barley. Arrhenius (1) showed that silica cannot replace phosphate as a nutrient; he attributed the increased phosphorus uptake resulting from applications of silica to an increase in the solubility of soil phosphate.

Densch and Steinfatt (11) suggested that soluble or colloidal silicates increase phosphorus uptake only when phosphate is present in a poorly available form. They noted that crystalline silica, no matter how finely ground, is useless in the soil and that silica affects phosphate availability only when the silica is colloidal. In an experiment with barley in Mitscherlich pots containing mixtures of sand and soil, Dix and Rauterberg (12) also showed that silica cannot be regarded as a substitute for phosphate in plant nutrition.

Work along similar lines, with generally similar results, was reported by Germanov and Taranovskaya (14, 15, 30) on unstated crops on Russian podzolic and red loam soils, and by Okawa (26) on rice crops in Japan. Rice, however, is particularly sensitive to silica, whose presence increases its resistance to "blast disease".

In the United States, Raleigh (28), working with soils from widely separated locations (pH 4.8 to 8.5), showed that applications of sodium and potassium

silicates increased uptake of phosphorus only from soils with low or intermediate phosphate levels. Silicates were ineffective on soils highly deficient in phosphorus or heavily treated with phosphate. Soil pH did not appear to affect results with sodium or potassium silicates, but calcium silicate may have been more effective on acid than on neutral soils.

The nature of the silicate-phosphate relationship was clarified further by Toth (31), who showed that dressings of calcium and magnesium silicates increased yields of barley and rye grass through displacement of phosphate from soil. In work with Houston black clay, Laws (21) observed that silicate treatment increased the water-soluble and citrate-soluble phosphate contents of the soil and decreased the quantity of phosphate it could adsorb from a dilute phosphate solution (about 30 p.p.m. of phosphorus). Sodium silicate was more effective than potassium silicate in increasing the solubility of soil phosphate, in agreement with Raleigh's (28) data.

In a more elaborate study of the chemical reactions between silicate and phosphate, Reifenberg and Buckwold (29) showed that silicate reversibly displaces orthophosphate from soils. They used 0.1 to 1*N* sodium and ammonium phosphate solutions (pH 3 to 11) and found that release of silicate increased with increase in either phosphate concentration or time. There was a marked minimum, however, at about pH 7.5. The pH effect was observed also in displacement of phosphate by 0.1*N* sodium silicate; release of phosphate decreased with increase in pH and became very small above pH 4.

Reactions between soluble silicates and various phosphate salts and minerals

were examined by Gile and Smith (16), Osugi and Saegi (27), and Küpper (20). Küpper studied reactions of 0.5 and 2% solutions of potassium silicates at pH's of 6.8 and below with such materials as di- and tricalcium phosphates, aluminum phosphate, basic slag, Rhenania phosphate, and rock phosphate that had been fused with silica. Results were the same when the materials were treated alone as when they were premixed with soil and sand. Silicate increased the dissolution of phosphate, the extent increasing with increase in time of contact, increase in concentration of the silicate solution, or lowering of pH. A lack of detailed information makes Küpper's results difficult to interpret. Some of the more insoluble materials may have contained occluded or adsorbed phosphate that was readily released to the solution without replacement of lattice phosphate. The results are in agreement with those of Gile and Smith (16), however, who concluded that silica gel causes some dissolution of rock phosphate.

Osugi and Saegi (27) reported similar results with tricalcium phosphate and phosphates of iron and aluminum, but they failed to characterize their materials. Bastisse (3, 4) found that silica always increased the solubility of the products of reaction of phosphate solutions with aluminum and iron hydroxides.

Although there is considerable evidence that colloidal silica and soluble silicates may release phosphate from certain adsorbed or precipitated forms, information on the mechanisms is meager. Sequestration of phosphate-adsorbing colloidal iron and aluminum hydroxides may be one of several effects of silica—a doubtful possibility, however, since the effect is not limited to acid soils.

The extent to which silicates can replace phosphate in lattice structure is not clear. Solid solution between calcium orthophosphates and orthosilicates is extensive in minerals from high-temperature melts, but these solid solutions apparently are not formed in aqueous systems. Replacement of the outer layers of phosphate by silicate is possible, but this replacement may be treated as an adsorption, and displaced phosphate is indistinguishable from that desorbed from surfaces of other minerals in the soil system.

Soluble silicates appear to be of little value as fertilizer materials; their small temporary effects are evident only in soils of low or intermediate phosphate status and are obtained at the expense of the soil phosphate reserve. Equal or better results can be obtained from dressings of a phosphate fertilizer.

Calcium Silicate Slags

High-temperature calcium silicate slags that contain less than 10% of phos-

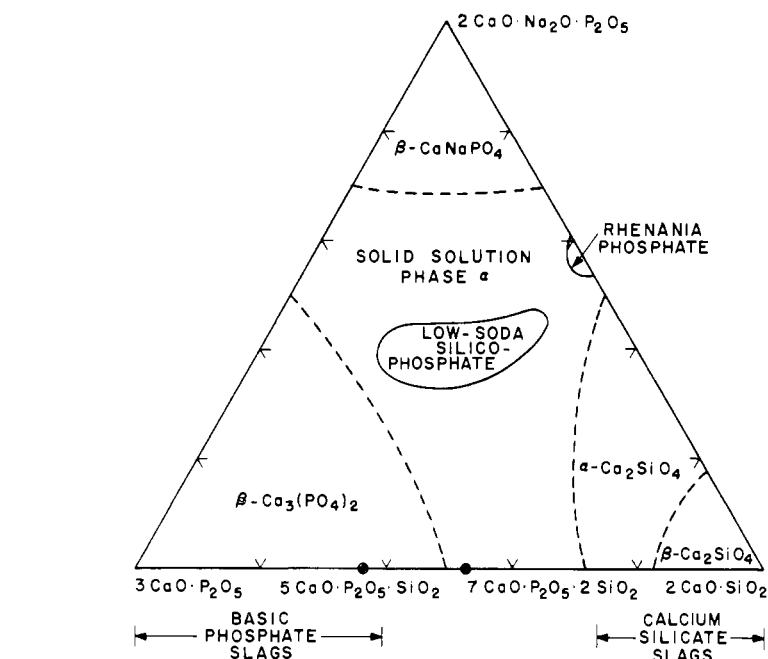


Figure 1. System tricalcium phosphate-dicalcium silicate-sodium dicalcium phosphate (22)

phoric oxide (representing about the maximum amount of tricalcium phosphate that can exist in solid solution in dicalcium silicate) are of relatively low solubility. The basic nature of such slags makes difficult an assessment of their effect on the phosphorus status of soil. Since slags raise the pH of an acid soil and supply calcium ions, which otherwise may be lacking, they serve primarily as liming materials, and the liming and fertilizing effects may be difficult to separate.

In a field comparison of the effects of nonphosphatic blast and steel furnace slags on wide ranges of crops and soils, Cooke (7) found no advantage of blast furnace slag over calcium carbonate, whereas steel furnace slag gave greater crop responses and larger phosphorus uptakes than either. Chemical and mineralogical characteristics of slags were not reported. Carter, Collier, and Davis (6) found Alabama blast furnace slags equal to or perhaps better than limestone on acid soils of the Alabama coastal plain.

Extensive greenhouse tests by MacIntire and coworkers (24, 25) related the effects of a slag to its physical properties and chemical composition. Quenched low-alumina electric furnace slag was more effective than an equal weight of limestone of similar particle size in dressings of up to 5 tons per acre. With larger dressings, however, 100-mesh slag produced toxic symptoms, perhaps because of its fluorine content. Applications of 10-mesh slag at the same rate were not toxic. Unquenched (crystalline) slag was beneficial on acid soils at almost any rate of application,

although it was less effective in raising the pH of soil. Increase in aluminum content of a slag decreased its effectiveness markedly (25), probably because of the presence of insoluble aluminum silicates.

A slag from the electrothermal production of phosphorus proved as effective as limestone in raising the pH of very acid Mississippi soils when Jones and Edwards (19) compared them on the basis of their calcium contents. The 1.3% of phosphoric oxide in the slag was more readily available to plants than an equivalent amount of superphosphate applied with limestone. Phosphate in the slag was probably present in solid solution in the calcium silicate or as silicocarnotite. In slag that has not been sufficiently defluorinated, or to which fluorspar has been added as a fluxing agent (a practice in the iron and steel industry) phosphorus may be present as fluorapatite whose availability is extremely low.

The difference between the effects of calcium silicate slags and soluble silicates on the phosphate chemistry of soil appears to be largely one of rate. Except for their phosphorus and possibly minor elements, slags are merely substitutes for limestone. When readily available in quantity, however, they may have considerable agricultural value.

High-Grade Phosphate Slags

High-phosphorus basic slags have been used extensively in Europe and in the United States close to steel centers, and although no account of any detailed, systematic, experimental work with these

materials is found in the literature, Crowther (9) has shown that their efficiency as phosphate fertilizers is closely correlated with their content of citrate-soluble phosphorus. The best slags are those which contain about 35% of phosphoric oxide and are composed principally of silicocarnotite. Slags containing more phosphorus lie within the tricalcium phosphate range and have a lower citrate solubility. Silica is sometimes added to blast furnace slags to ensure a final product of the silicocarnotite type.

Although the region of the calcium oxide-phosphoric oxide-silicon dioxide system that includes the basic slags is well explored, Barrett and McCaughey (2) interpret the physical chemistry of the basic slags in terms of the binary system dicalcium silicate-tricalcium phosphate—a simplification fairly close to the conditions usually met in practice.

Nagelschmidite ($7\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{SiO}_2$) and silicocarnotite ($5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$) appear in the system in addition to the two end members, and solid solution between adjacent members is extensive. Barrett and McCaughey report ranges of composition, expressed as weight ratio of phosphoric oxide to its sum with silicon dioxide, in which homogeneous solid solutions are formed with single predominant phases: dicalcium silicate, 0 to 0.2; nagelschmidite, 0.31 to 0.58; silicocarnotite, 0.71 to 0.80; and tricalcium phosphate, 0.89 to 1.0. The groups PO_4 and SiO_4 in each of these phases are similarly bonded with calcium ion and considered virtually interchangeable. A narrow region along the line tricalcium phosphate-dicalcium silicate is, with minor exceptions around other compounds, unique in the formation of solid solutions in the system calcium oxide-phosphoric oxide-silicon dioxide.

Slags formed under conditions suitable for the formation of apatites are less desirable as fertilizers. In their studies of defluorination of phosphate rock, Hill, Hendricks, Jefferson, and Reynolds (18) showed that an apatite phase of low solubility was formed when melts with compositions in the silicocarnotite region were cooled slowly, especially in a moist atmosphere. Quenching of the melt inhibited formation of apatite and maintained a high citrate solubility. The practice of adding fluorspar to the furnace to lower the viscosity of slag is particularly undesirable in this regard, as considerable fluorapatite will be formed with resultant decrease in the value of the slag as a phosphate fertilizer.

The fertilizer value of basic slags thus depends principally upon the chemical state of phosphorus. Silicate content appears to be of importance only insofar as it determines the predominant phosphate phase. This also appears to be true in products from processes similar to those used to make Rhenania or silicophosphate fertilizers. These products, made by heating phosphate rock with sand and soda ash at about 1100° to 1200° C. in an atmosphere of steam, are agronomically similar to basic slags. The chemical relationship between these compounds (complex solid solutions in the system tricalcium phosphate-dicalcium silicate-sodium dicalcium phosphate) and the basic slags is illustrated in Figure 1, which is adapted from Lea and Nurse (22) who investigated the system in some detail. The use of various materials of this type in Europe has been discussed by Cooke (8), but experience in the United States appears to be limited to studies of Rhenania phosphate as described by Brenes (5).

Conclusions

Dressings of colloidal silica or soluble silicates improve the nutrient status of soils of moderate or low phosphate status through exchange reactions in which silicate ion displaces adsorbed phosphate ion from soil colloids.

The principal action of low-phosphate blast and electric furnace slags appears to be that of liming agents. Soluble silicate released by slags has little effect on the phosphate status of soil, although it may displace small amounts of phosphate over long periods.

The fertilizing effect of high-phosphate basic slags and silicophosphates is due almost entirely to the orthophosphate ion they supply. The soil chemistry of these materials is influenced little by their silicate content, except on acid soils where they have some liming effect.

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