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A New Explanation of what Happens to Superphosphate in Limed Soils

University of Tennessee Agricultural Experiment Station

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A NEW EXPLANATION OF WHAT HAPPENS TO SUPERPHOSPHATE IN LIMED SOILS

By

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A NEW EXPLANATION OF WHAT HAPPENS TO SUPERPHOSPHATE IN LIMED SOILS

W. H. MacIntire

INTRODUCTION

This bulletin gives a new explanation as to what happens to additions of superphosphate in limed soils. The explanation is based upon results obtained during some 14 years of experimentation as to the chemical transitions and solubility changes that ensue when superphosphates are mixed with calcic, magnesic, and dolomitic liming materials, before and after incorporation with soils. The present text deals with the successive chemical transitions that take place when (a) superphosphates are mixed with liming materials outside the soil, and (b) when superphosphates are incorporated with limed mineral soils of the humid region. An effort is made to explain the successive formation of phosphates of decreasing solubility in limed soils, and the relation of these changes to the fact that only a fraction of a superphosphate addition is recovered through plants grown on such soils.

SUPERPHOSPHATE ADDITIONS TO UNLIMED AND LIMED SOILS

Most soils of the humid region have been depleted of their supplies of the basic elements and have become sour, a condition registered chemically in terms of pH below 7. Substantial additions of superphosphate to distinctly phosphorus-deficient sour soils may fail to bring appreciable increase in crop yields. In general, judicious liming increases plant response to superphosphates. In contrast, liming generally decreases the immediate response to raw phosphate.

The P_2O_5 content of superphosphate is chiefly in water-soluble combinations that are generated when raw rock phosphate is acidulated, or converted to an acidic product, with either sulfuric or phosphoric acid. The practice of converting bones and raw rock phosphate to the product known as acid phosphate, or superphosphate, marked the beginning of the present gigantic fertilizer industry.

It was supposed that the water-soluble phosphates would diffuse throughout the soil and there continue in the form applied. This supposition has been proved erroneous. The soluble phosphates are fixed quickly and held tenaciously by sour soils, and therefore do not diffuse throughout the soil as do the soluble neutral nitrate, chloride, and sulfate fertilizer salts. It has been taught that the capacity of a sour soil to convert soluble phosphates to insoluble combinations is governed by the form and amount of its iron and aluminum com-

plexes. This capacity to convert soluble P_2O_5 into insoluble forms is diminished by liming. But even when the capacity of a soil to fix the P_2O_5 of superphosphates is lessened by the conventional practice of liming, the amount of P_2O_5 recovered in the crop may represent only a fraction of the amount added. An adequately prelimed soil will promote the conversion of superphosphates to tricalcium phosphate, or "bone phosphate of lime", which has been supposed to be the ultimate form of calcium phosphate developed in the soil. Conversion to this form, which corresponds to the composition of bone, has been considered responsible for a distinct diminution in the availability of soluble P_2O_5 supplied to limed soils, even though steamed bone has been recognized as a good phosphatic fertilizer.

We know, however, that a *true* precipitated tricalcium phosphate, and also steamed bone, has a high degree of chemically measured "availability", in comparison with that of the raw mineral rock phosphate, or "floats", and the so-called "colloidal" phosphate. Hence, were tricalcium phosphate actually the final product resultant from superphosphate incorporations in limed soils, there would be continued benefit to plant growth and an extended P_2O_5 recovery. We recognize, now, however, that precipitated tricalcium phosphate, and also "bone phosphate of lime", is a material quite different from apatite, the natural geological combination of tricalcium phosphate and calcium fluoride occurrent in rock phosphate. The correlation of the results summarized and interpreted in this bulletin emphasizes that distinction and points to a new explanation as to the final calcium phosphate that develops from superphosphate in a limed soil.

EARLIER OBSERVATIONS

To develop a clear picture of the changes that the water-soluble P_2O_5 content of superphosphate undergoes in limed soils, it seems appropriate to recount earlier teachings and then discuss those chemical transitions that take place when water-soluble calcium phosphate and liming materials are brought together outside the soil. It is helpful to remember that (a) one unit of P_2O_5 in combination with one of lime gives a water-soluble phosphate, (b) one unit of P_2O_5 with two units of lime gives an intermediate water-insoluble dicalcium, or dicalcic, phosphate that is readily soluble, however, in the carbonated water of the soil and highly available to plants, and (c) one unit of P_2O_5 with three units of lime gives a tricalcium phosphate, similar to bone phosphate, of less solubility.

Fertilizer manufacturers long have known that limited quantities of limestone could be admixed with superphosphate advantageously to diminish its tendency to cake and become sticky, and to neutralize its free-acid content and thereby prevent disintegration of containers. Some 25 years ago, one state agency recommended that superphos-

phate be mixed with limestone before incorporation with soil, whereas another agency in the same state controverted that recommendation. The differential behaviors of limestone and dolomite in their mixtures with superphosphates and the need for the nutrient magnesium supplied by dolomite had not been pointed out, and therefore were not an issue in the controversy.

A commercial chemist demonstrated that ordinary superphosphate can be mixed, or "cut", with substantial proportions of high-calcic limestone in small piles without appreciable detriment to P_2O_5 "availability". Later, another demonstrated the same to be true for small mixtures of the concentrated, or "triple", superphosphate. At one experiment station, workers conducted experiments with home-scale mixtures of limestone and superphosphate, and concluded that the limestone induced a loss of chemically measured P_2O_5 "availability". A similar conclusion was drawn at another station from laboratory-scale experiments with admixtures of precipitated calcium carbonate.

Prior to 1919, no distinction had been made between limestone and dolomite as conditioning agencies for commercial phosphatic fertilizers. The Tennessee Experiment Station then suggested that the less reactive dolomitic limestone might be preferable to high-calcic limestone as a conditioning agency and to replace sand as a "filler". The suggestion for the inclusion of dolomite then was adopted by one fertilizer company. One of the larger fertilizer corporations compared the activities of several dolomites in admixtures with superphosphate in 500-pound piles, and no reversion was encountered. Shortly thereafter came the classical experiments that demonstrated the fertilizing value of magnesium, and it is now recognized that most soils of the Coastal Plain are deficient in that element and respond to additions of it. Later, it was shown that substantial quantities of readily soluble dimagnesium phosphate are generated during the aging of mixtures of superphosphate and dolomite. These findings and the recognition of the need to offset the tendency of mixed fertilizers to cause soil acidity stimulated interest in and brought an appreciation of the merits and value of inclusions of dolomite. This type of limestone now is used extensively as a dual-purpose material in the manufacture of improved commercial fertilizers. It is included in proportions computed to render a fertilizer "non-acid forming".

LATER EXPERIMENTAL WORK

In 1927, laboratory investigations were initiated at the Tennessee Station to study the reactions that occur in mixtures of ordinary superphosphate with ordinary, or high-calcic, limestone and marble, and with dolomitic limestone and dolomite. The results indicated that chemical activities had ceased in small piles of fertilizers containing compatible quantities of limestone or dolomite, after a frac-

tion of the water-soluble phosphate content had gone to the readily available dibasic forms. The initial moisture of the superphosphate and the water produced by the reactions were transformed chiefly into water of chemical combination by the dicalcium and dimagnesium phosphates generated in the mixtures. Hence, the resultant mixtures contained variant proportions of water-soluble acidic phosphates, water-insoluble dibasic phosphates, and undecomposed limestone or dolomite, in a state of non-reactivity. The proportions of these several components of the cured mixtures varied with different starting proportions, moisture, size of the mixtures and their moisture content, and temperature and humidity prevalent during the period of curing. It is emphasized that although dicalcium phosphate, as well as dimagnesium phosphate, is sparingly soluble in ordinary water, it is highly soluble in the carbonated water of the soil and is the form utilized by plants.

A considerable decrease in phosphate availability may occur when mixtures of superphosphate and high-calcic limestone are cured, or aged, in large piles, even when the quantity of admixed limestone is only a fraction of that requisite for complete conversion of the water-soluble phosphates to water-insoluble forms. This comes about as the ultimate effect of successive changes that induce complete reversion in localized zones close to the surfaces of the dispersed limestone particles. It will be shown, however, that no loss of phosphate availability occurs in mixtures of limestone and superphosphate in piles suitable in size for home mixing, even when the mixtures include large proportions of limestone.

Reactions between superphosphates and limestone or dolomite produce carbon dioxide, the colorless soda-fountain gas. The evolution of this gas from continuously agitated and aerated water suspensions of water-soluble calcium phosphate and limestone or dolomite was used to measure the rate and extent of the formation of the dibasic and tribasic phosphates. The suspensions initially were composed of one part of water-soluble calcium phosphate and 20 parts of either limestone or dolomite. The rapid reaction of the soluble phosphate with the limestone in the water suspensions caused a precipitation of the solid dicalcium phosphate. Continued agitation and removal of the liberated gas caused a slow and incomplete conversion of the solid dicalcium phosphate to the less soluble tricalcium phosphate during a period of 28 days. In the parallel suspensions of dolomite in water, however, the transitions almost terminated when the initial water-soluble calcium phosphate had been converted to the dicalcium and dimagnesium phosphates.

The next step was to determine how rapidly and to what extent the formation of the tribasic phosphates can be induced in mixtures of ordinary superphosphate with limestone and with dolomite. Since dicalcium phosphate is formed quickly in superphosphate-limestone

mixtures—and likewise in corresponding dolomite mixtures, although with less rapidity, and to a less extent—pure dicalcium phosphate was used as the starting material in separate experimental mixtures with 100-mesh limestone and with 100-mesh dolomite. The respective quantities of admixed limestone and dolomite were 110 percent beyond those requisite for complete conversion of the dicalcium phosphate to the tribasic phosphates. The dry mixtures then were slurried with distilled water and the slurries were allowed to dry, after which the mixtures were subjected to frequent wettings during the next 12 months. The small mixtures, therefore, were much more moist than large piles of superphosphates and limestone would be under ordinary conditions, but the dissipation of heat of chemical reaction was much more rapid from the small mixtures. The accelerative influence of moisture upon the conversion of dicalcium phosphate to the more basic tricalcium phosphate was greater in the small piles, whereas the accelerative influence of elevation in temperature was less.

The rate of the conversion of the dibasic phosphates to tribasic phosphates in these laboratory mixtures was established by periodic determinations of the residues of limestone and of dolomite. Complete conversion to the tribasic phosphates was never attained. The high-calcic limestone caused 30 percent of the dicalcium phosphate to go to the tricalcium form during the first month, and only 60 percent of the possible conversion had occurred at the end of 12 months. In the corresponding periodically wetted dolomite mixtures, the conversion of the dicalcium phosphate to tribasic phosphates during the first 6 months was 6 percent of complete conversion and only 26 percent at the end of 12 months.

When the concentrated, or so-called "triple", superphosphate came into substantial production, it was thought advantageous to "cut", or dilute, and neutralize that superphosphate with either limestone or dolomite, *at the farm*. The objectives were (a) to give a mixture that could be incorporated with farm implements intended for the incorporation of ordinary superphosphate, (b) to minimize undesirable fixation of P_2O_5 by soil compounds other than those of calcium, (c) to prolong the occurrence of the dibasic forms of phosphate in the soil, and (d) to obviate the danger of a toxic effect of acidic fluorides upon seed germination.

Mixtures of one part of the concentrated superphosphate and two parts of either limestone or dolomite, therefore, were made in the laboratory and also in piles of 1500 pounds and of 9 tons. The admixed limestone and dolomite induced 90 and 80 percent respective conversions to the dibasic phosphates in the 1500-pound piles during the initial week. Practically no loss of P_2O_5 availability and no caking had resulted in the shovel-turned air-cooled piles after the first 3 days, and even after aging for 6 months.

Then came the idea that it would be well to expedite the formation of the dibasic phosphates by the use of *wetted* limestone and dolomite to obtain, quickly, self-drying mixtures. These would be composed of (a) dicalcium phosphate and a major proportion of undecomposed limstone and (b) dicalcium and dimagnesium phosphates and a major proportion of undecomposed dolomite. Five hundred pounds of the 45-percent superphosphate was added to 1000 pounds of limestone or dolomite, thoroughly wetted, on the apron of a concrete mixer. The mixture was dumped into the concrete mixer and churned 2 minutes or more. When the 9-ton piles thus obtained were cured 6 days, the conversion of water-soluble phosphates to dibasic phosphates was about 90 percent for the high-calcic limestone mixture and 80 percent for the dolomitic limestone mixture. The wetted mixtures rapidly attained a relatively dry granular condition, as the result of the chemical uptake of water by the generated dibasic phosphates. One county agent found it advantageous to transfer the wetted mixtures immediately to bags filled to 85-percent capacity, and without stacking, and then "up-end" the bags twice daily for several days to hasten curing and to preclude caking. Since the heat resultant from the chemical reactions within the 9-ton limestone mixture was not dissipated quickly during its storage in bins, some "unavailable", or citrate-insoluble, P_2O_5 developed in the centers of the bin-stored piles, whereas practically no decrease in P_2O_5 availability occurred in the parallel dolomite mixtures.

DISCOVERY OF THE CAUSE OF REVERSION IN LIMED SUPERPHOSPHATES

The next step was a trial of similar mixtures of triple superphosphate with 100-mesh calcium silicate slag, a by-product from rock phosphate reduction furnaces operated by the Tennessee Valley Authority at Wilson Dam and by commercial corporations in Tennessee and in Florida. The probable utility of this slag was suggested by experiments conducted at the Tennessee Station in 1914, which showed that the liming value of a calcium silicate mineral is equal or even superior to that of an equivalent amount of limestone. The extraneous solids of the rock phosphate are contained in the slag, which has a liming value equal to a limestone of about 80-percent purity. The lime content of the slag is in chemical combination with silica, or quartz, instead of the combination with the carbon dioxide of limestone. Calcination causes limestone to lose its carbon dioxide content of 44 percent, leaving 56 percent of burnt lime. Calcination of a mixture of lime and quartz causes these two materials to combine and form a molten slag, similar to glass, which shatters upon being quenched. The slag contains 6 percent of calcium fluoride, whereas limestone contains practically none.

When 2 parts of the glassy slag were mixed with one part of the concentrated superphosphate in small piles, 30 percent of the possible formation of dicalcium phosphate occurred. These small mixtures quickly became so dry as to inhibit further chemical changes, and hence there was no harmful effect. This was not true for the corresponding mixtures in which *wetted* slag was used in the manner followed when wetted limestone and dolomite were used. The phosphate content of the wetted-slag mixtures underwent a progressive and extensive decrease in chemically measured "availability". The effect induced by the admixed slag exceeded that induced by either limstone or mineral calcium silicate in corresponding mixtures. It was apparent that considerable quantities of a type of tricalcium phosphate of unusually low solubility had been formed by reaction between the generated dicalcium phosphate and the excess of the alkaline slag.

Because of the unusually low solubility of the calcium phosphate formed in the slag-superphosphate mixtures, it was concluded that the tricalcium phosphate formed in the mixtures had proceeded to react with calcium fluoride to form calcium fluorphosphate, a compound analogous to the mineral apatite of rock phosphate. The exceedingly insoluble ultimate calcium phosphate, namely, calcium fluorphosphate, can be designated as a combination between 3 formula units of tricalcium phosphate and one formula unit of calcium fluoride, or 12 parts to one part by weight.

This conclusion was supported by chemical analysis and X-ray examination, which showed that the citrate-insoluble residues of analytical charges of the mixtures had a high content of calcium fluorphosphate. It was natural to attribute the formation of the insoluble phosphate chiefly to the relatively large fluoride content of the slag. It was found, however, that considerable proportions of the same fluorphosphate compound were formed during the aging of similar mixtures of superphosphate and the fluoride-free calcium silicate mineral, wollastonite. Related studies showed that the fluorphosphate, or precipitated apatite, developed also when either ordinary or concentrated superphosphate was mixed with either of several other fluoride-free basic calcic compounds. When an experiment conducted elsewhere was repeated, it was found that a substantial decrease in the P_2O_5 availability of superphosphate occurred when the superphosphate and ammonium sulfate were mixed with calcined rock phosphate, which is essentially fluoride-free tricalcium phosphate and highly available. The reversion of superphosphates was found to occur without inclusion of the ammonium sulfate in their mixtures with powdery rock phosphate of low fluoride content. But no reversion occurred when various fluoride-free experimental superphosphates were substituted for commercial superphosphates in mixtures of the same powdery defluorinated rock phosphate calcine. Moveover, no develop-

ment of unavailable phosphate occurred during the curing of similar mixtures of fluoride-free superphosphates and rational proportions of either hydrated lime, calcium cyanamid, or limestone; or with dolomite, either alone or in its joint use with gaseous ammonia.

Further laboratory work demonstrated that the precipitated reagent type of tricalcium phosphate, corresponding to the phosphate formed slowly from superphosphate additions to well-limed soils, is converted to calcium fluorphosphate, or apatite, in moist mixtures with finely divided calcium fluoride. The conversion was hastened greatly when the moist mixtures were heated gently, and the complete transition of tricalcium phosphate to calcium fluorphosphate in these mixtures was established by chemical tests and by microscopic examination. The transition was registered also by a 50-percent decrease in the P_2O_5 uptake by rye seedlings when a gently heated mixture of tricalcium phosphate and calcium fluoride was compared with a similar unheated mixture in soil cultures.

THE ROLE OF FLUORINE IN PROCESSED FERTILIZERS

Some fluorine is evolved when rock phosphate is treated with either sulfuric or phosphoric acid to produce superphosphate, but most of the fluoride content of the starting raw rock phosphate is present in its superphosphate derivative. When adequate admixtures of basic calcic compounds are made, the fluoride content of superphosphate is capable of inducing reversion of the entire P_2O_5 content of the superphosphate to calcium fluorphosphate. The formation of this ultimate phosphate during the curing of processed superphosphates and mixed fertilizers is accelerated and extended by basicity, moisture, and relatively slight elevation in temperature. Hence, with a given addition of a calcic type of liming material, the more moist the mixture, the higher the humidity, the larger the piles, and the longer the curing period, the greater is the development of calcium fluorphosphate and resultant decrease in P_2O_5 availability.

The formation of fluorphosphate is responsible also for the development of unavailable, or citrate-insoluble, P_2O_5 during the curing of large piles of commercially ammoniated superphosphates, in which additional reactions generate tricalcium phosphate. This ammonia-generated tricalcium phosphate then reacts with adjacent particles of calcium fluoride to form calcium fluorphosphate and cause reversion. The reversion reaches serious proportions when ordinary superphosphate of high calcium sulfate content is ammoniated, and it is necessary, therefore, to restrict the amount of injected ammonia to a fraction of the amount the superphosphate can absorb. No development of citrate insolubility, or reversion, occurred, however, when fluoride-free experimental superphosphates, with and without additions of calcium sulfate, were ammoniated completely.

OTHER EVIDENCE AS TO THE FORMATION OF CALCIUM FLUORPHOSPHATE

The correctness of the conclusion as to the ultimate formation of fluorphosphate in mixtures of superphosphates and liming materials outside of the soil has been established through several lines of attack. Moreover, the geological formation of rock phosphate has been ascribed to the affinity of calcium phosphate for fluorides and formation of mineral apatite through the reaction between bone phosphate deposits and the fluorides carried by percolating ground waters. The probability that the same thing would occur slowly in mixtures of superphosphates and liming materials at ordinary temperatures should have been reasoned from the fact that a substantial percentage decrease in the availability of the phosphate content of basic slag occurs when the mineral fluorspar, or calcium fluoride, is added to increase the fluidity of the molten phosphatic slag, the well-known "basic slag". The decided affinity of tricalcium phosphate for calcium fluoride has been capitalized by the use of activated bone filters which remove fluorides completely from natural waters and by the capacity of suspended tricalcium phosphate and of joint additions of phosphoric acid, hydrated lime, and clay to effect the same result. Conversely, the scantly soluble mineral apatite of rock phosphate is converted to a tricalcium phosphate of high availability when the fluorine content of rock phosphate is expelled by either calcination or the fusion procedure utilized by the TVA at Wilson Dam.

INTERPRETATIONS

The nature and rate of the several successive phosphate transitions—water-soluble to dibasic to tribasic to fluorphosphate—that occur outside the soil can be determined with some degree of accuracy. It is established that in moist mixtures of superphosphates and liming materials at ordinary temperatures (a) the transition of the water-soluble phosphates to completely "available" dicalcium phosphate is exceedingly rapid, (b) the successive transition of the generated dicalcium phosphate of high degree of availability to tricalcium phosphate is very slow, and (c) the subsequent formation of calcium fluorphosphate of low solubility is the ultimate result.

The next and more difficult step is to bring the laboratory findings into harmony with related soil studies. With ideal conditions as to adequate soil content of calcium and magnesium as either carbonates or silicates, it seems reasonable to conclude that directly incorporated dicalcium phosphate will persist in the soil. So long as this phosphate continues, no formation of calcium fluorphosphate occurs.

The natural acidic iron and aluminum compounds that render phosphates insoluble are altered chemically by liming and deprived of their ability to precipitate, or fix, the soluble phosphates of incorporated superphosphate. Laboratory findings and studies else-

where demonstrated that no fixation reactions between those oxides and dicalcium phosphate occur in the carbonated water solutions of limed soil. In a soil adequately limed and subsequently treated with superphosphate, there is a tendency toward the gradual formation of tricalcium phosphate, because of the continuous contact between generated dicalcium phosphate and the carbonates and silicates of calcium and magnesium. When tricalcium phosphate is dissolved in the soil water, however, the result is a solution containing dicalcium phosphate and calcium bicarbonate. Since the component fluorides of incorporated superphosphate are not leached readily from a soil limed with ordinary limestone, the formation of tricalcium phosphate in a limed soil that still retains the added fluorides should be followed by the transition of that phosphate to the fluorphosphate, just as in the mixtures of tricalcium phosphate and calcium fluoride outside the soil.

INDICATIONS FROM SEEDLING CULTURES

The evidence from the experiments with mixtures and suspensions of superphosphates and liming materials seems to warrant the conclusion that the transition of dicalcium phosphate to tricalcium phosphate in the soil is much slower than it has been our custom to assume. The problem is: Does the transition of the water-soluble phosphate content of superphosphate stop after the quickly generated dicalcium phosphate passes to the slowly formed tricalcium phosphate in limed soils, or does the last-mentioned phosphate go on to the ultimate calcium fluorphosphate? Information as to this query was obtained by plant cultures.

When soils were aged after being limed with limestone and with the calcium silicate slag that contained fluorides and then phosphated with 90-day-cured mixtures of a special fluoride-free superphosphate and fluoride-free powdery calcium silicate and seeded to rye, the amount of P_2O_5 taken up by the plants was twice as much as that taken up from a correspondingly cured mixture in which the slag was substituted for the fluoride-free calcium silicate. Futhermore, when the same two prelimed soils received incorporations of tricalcium phosphate, alone and as a component of its 6-day mixture with calcium fluride in the weight ratio of 12 to 1, the mean plant uptake of P_2O_5 from the phosphate-fluoride mixture was less than half the uptake from the straight addition of tricalcium phosphate.

In another experiment, it was found that no decrease in P_2O_5 uptake by the rye seedlings was caused by a prior addition of calcium fluoride to the soil, when the subsequently added P_2O_5 was in the form of dicalcium phosphate. In this experiment 3 soils were limed and aged, and then were treated with calcium fluoride, at rates equivalent to the fluorine content of 2-ton and 4-ton additions of slag, and again aged. Equivalent quantities of dicalcium and tricalcium phosphates then were incorporated, and the soils were aged once more before

seeding. The effect of the preaddition of calcium fluoride was to decrease decidedly the P_2O_5 uptake from the subsequent incorporation of tricalcium phosphate, whereas that unfavorable effect did not occur in the soils treated with dicalcium phosphate.

THE NEW EXPLANATION

The cumulative findings of some 14 years seem to warrant a new explanation as to what happens to superphosphate after its addition to limed soil. We have adequate evidence that the dicalcium and tricalcium phosphates, and also the corresponding phosphates of magnesium, are readily available to plants, whereas calcium fluorphosphate is not. The mere conversion of the water-soluble phosphates of superphosphate to dicalcium phosphate, and on to tricalcium phosphate in the soil, probably would not mean a serious loss of available P_2O_5, provided the soil content of calcium carbonate was not so great as to exert a repressive effect upon the solubility of other soil nutrients—magnesium, potassium, boron, manganese, and iron—and a tie-up of the carbon dioxide in the soil system. Heavy liming is apt to generate an unnecessary and undesirable quantity of calcium salts, and a high concentration of any soluble calcium compound in the soil solution tends to diminish the solubility of basic calcium phosphates. The unavailability of tricalcium phosphate in soils that contain large quantities of other calcic compounds can be accounted for by the fact that the soil water will dissolve those compounds readily and thereby lose most of its capacity to dissolve tricalcium phosphate. Furthermore, undue alkalinity diminishes the capacity of the plant rootlets to imbibe calcium phosphate.

The imposition of certain drastic conditions upon soluble phosphates in the laboratory will bring about the formation of a particularly basic compound, calcium hydroxyphosphate, or hydroxy apatite, which has a low degree of availability. But no evidence has been advanced to show that hydroxyphosphate is generated under conditions encountered in the rational premixing of phosphates with either limestone or dolomite or in the practice of phosphating and liming the soils of the humid regions. It has been suggested also that heavy liming will affect phosphate utility indirectly by causing a decrease in the availability of the boron content of the soil. Moreover, accumulations of data at this Station have demonstrated the fact that liming tends to exert a similar effect upon the solubility of soil potash, both native supplies and that added as fertilizer salts.

An explanation as to what becomes of superphosphate drilled into the soil is advanced, therefore, upon the basis of the results obtained from mixtures, suspensions, and filtrations outside the soil, and from evidence as to the uptake of P_2O_5 from the soil by seedling cultures. When premixtures of superphosphate and *wetted* limestone or dolomite are cured and incorporated, or when superphosphate is incorporated

with either an adequately prelimed soil or one naturally calcareous, the water-soluble phosphates pass successively to dicalcium phosphate, tricalcium phosphate, and calcium fluorphosphate. This succession is in the inverse order of solubility and the availabilities of these phosphates to growing plants. The formation of the calcium fluorphosphate end-product through reaction between tricalcium phosphate and calcium fluoride is hastened by the alkalinity, or elevation in pH, induced by an excess of calcic liming materials. The dimagnesium phosphate generated in mixtures of superphosphate and dolomite apparently does not react directly with calcium fluoride, since no experimental evidence has indicated the formation of magnesium fluorphosphate.

The question arises as to the source and adequacy of the calcium fluoride essential for the ultimate transition of the water-soluble P_2O_5 of superphosphate to calcium fluorphosphate in the soil. Superphosphates derived from domestic rock phosphates always contain fluorides in excess of the amounts necessary to effect the complete reversion of their soluble P_2O_5 content to the form of calcium fluorphosphate, which is analogous to the apatite present in the raw rock. Rainwaters collected at the Tennessee Station have shown fluoride content. With one possible exception, all Tennessee soils analyzed have shown appreciable content of fluorides, which, however, may be already in the form of the natural apatite, and therefore inactive toward added phosphates. In a 4-year lysimeter experiment, only a scant removal of substantial additions of fluorides had been effected by the rainwater leachings from a soil moderately limed with high-calcic limestone, and the ability of the added fluoride to form calcium fluorphosphate within the soil was offered as a possible explanation of the retention of the added fluoride.

Outgo of fluorides was accelerated by the magnesium supplied by dolomitic limestone. Dolomite therefore may diminish the potentiality of the fluoride content of incorporated superphosphate to induce the ultimate formation of calcium fluorphosphate in the soil. It is quite possible that this effect of added magnesium upon the solubility of fluorides and their consequent removal by rainwater leaching exerts an influence upon phosphate availability in the soil, and may be responsible, in part, at least, for the fact that dolomite increases the movement of phosphates within the soil and sometimes proves more beneficial than equivalent quantities of ordinary, or high-calcic, limestone. Moreover, dolomite supplies less calcium than does an equivalent quantity of limestone in reactions with superphosphates, and it therefore generates a smaller quantity of dicalcium phosphate for successive conversions to tricalcium phosphate and calcium fluorphosphate. As stated, dolomite also generates dimagnesium phosphate, which apparently does not react with calcium fluoride to form phosphates of meager solubility.

The probability and extent of the formation of calcium fluorphosphate within the soil is also decreased by the incorporation of cured moist mixtures of superphosphate and either limestone or dolomite. The dibasic phosphates formed in such mixtures will not migrate so readily in the soil and are less soluble than the fluoride components, which will be diffused from intimate contact with the subsequently formed solid particles of the more basic tricalcium phosphate. Another advantage is that the limestone or the dolomite of such premixtures eliminates the toxic effect that the fluorine compounds of unneutralized concentrated superphosphate may exert upon seed germination.

The incorporation of rational quantities of liming materials will convert a sour soil into a system that will supply calcium to propel those successive phosphatic conversions that have been demonstrated as occurrent in limestone-superphosphate mixtures outside of the soil. Conditions conducive to the ultimate formation of calcium fluorphosphate are created when a prelimed soil is phosphated by superphosphate at economic rates. The development of that insoluble compound in limed and phosphated soils would be slow but certain. The grain size of the calcium fluorphosphate formed from superphosphate drilled into a limited zone of a limed soil would be greater than the grain size of fluorphosphate formed from incorporations of broadcast superphosphate. This means that the solubility of the fluorphosphate derived from incorporations of superphosphate in limed soils would exceed the solubility of the geologically formed mineral calcium fluorphosphate, or apatite, of pulverized rock phosphate. Such disparity in degree of solubility is measured definitely by chemical methods and also by plant growth. The development of calcium fluorphosphate and the scant solubility of that compound may not be the sole cause for the gradual diminution in the availability of superphosphates to plant growth in limed soils, but it certainly contributes to that diminution. It seems clear that the best joint usage of superphosphate and liming materials is one that promotes the continued occurrence of P_2O_5 in the form of dibasic phosphates.

Upon the assumption that the formation of calcium fluorphosphate in limed soils is the dominant factor in the economic response to and recovery of P_2O_5 from superphosphate additions to limed soils, the question arises as to the feasibility and economy of the production of fluoride-free phosphates for use not only in fertilizers, but also as a source of dicalcium phosphate for livestock.

It is hoped that the problem will be clarified by further studies of the effect of additive fluorides upon the availability of P_2O_5 within the soil and upon the fluorine content of various crops, and by lysimeter experiments to determine the removal of soil fluorides by rainwater leachings.

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