SOME ASPECTS ON PHOSPHATE FIXATION AND REVERSION IN CALCAREOUS SOILS AS RELATED TO THE USE OF SUPER-PHOSPHATE FERTILIZER

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The fixation, reversion, and adsorption of phosphorus in soils when applied, as superphosphate fertilizer is a problem which has confronted Soil Scientists, Agronomists, and the fertilizer industry since the inception of superphosphate fertilizer.

Some early work on the subject generally developed the opinion, with some exceptions, that fixed or reverted phosphorus was a complete loss in the soil insofar as availability to plants was concerned. Later work has not supported this idea entirely and at the present time the subject seems to be a controversial one.

In presenting some of the recent aspects on this subject, I will attempt to discuss it from a practical view point such as would concern and influence the user of superphosphate fertilizers.

Definitions

The terms fixation and reversion have been confusing since they have, in many cases, been used to refer to the same. I would define these terms as follows:

Fixation - This term is usually used in the sections where the soils are acid, and implies a chemical reaction in the soil in which the phosphoric acid reacts with some element wuch as aluminum or iron to form a new product which is insoluable and thereby fixed.

<u>Reversion</u> - This term is usually used in connection with soils high in lime, and basic in reaction - calcareous soils. It implies a reversible chemical reaction whereby the phosphoric acid may combine with calcium and revert from a soluable to a more insoluable product. Just exactly what takes place and the extent to which it takes place is still a **question**.

<u>Absorption</u> - This term refers to the attachment of the phosphoric acid molecules to the colloidal particals of the soil without any particular chemical changes occurring. We call it anion adsorption. Some use both the terms fixation and reversion to refer to a changing process in the soil whereby they assume the phosphate is first fixed or held to the colloids and then gradually reverted over a period of time. In this report I will use the term reversion, as I feel it is more applicable to our intermountain conditions.

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Importance of Reversion

If reversion of superphosphate takes place, it is of importance to both the consumer and manufacturer. It will influence a number of fertilizer practices such as time of application, rate of application per acre, method of application and placement in the soil, and use of superphosphate with manure.

I felt that many of the opinions expressed and many of the recommendations made to consumers have been more or less assumptions which may or may not be supported by research work and are based on the theory that reverted phosphate in the soil is an entire loss insofar as being available for plant food. In developing this theory the fact that natural raw rock phosphate is not available, has been used a a criterion. The statement is made that the phosphate exists in the raw rock as tricalcium phosphate. This idea has come from the custom of the fertilizer trade to express the quality of phosphate rock in terms of Tricalcium phosphate equivalent of total phosphorus. They assume if phosphate rock is not available, then the tricalcium phosphate resulting from the reversion of superphosphate in the soil, is not available either. This is an erroneous assumption. Utah, Idaho, Arizona and other western experiment stations have shown that natural ground phosphate rock is not an available plant food.

In what form does the phosphate exist in natural Phosphate Rock?

The dictionary of fertilizer materials and terms, states, "The phosphate is found combined with lime and fluorine. Small amounts of iron and alumina are also present. The phosphorus is probably in the form of <u>fluor</u> -<u>apatite</u> in all commercial grades of phosphate rock produced in the United States. Apatite is a group of calcium phosphates containing fluorine, chlorine or the hydroxal group, either singly or together. Fluor - apatite is the best known of the apatites. $(ca_{10} (x_2) (po_4)_6(X_2))$ in the formula represents the flourine)

Dr. Sanchelli of the Davidson Chemical Corporation states, "The common but erroneous belief that Tricalcium phosphate is the phosphatic component of phosphate rock has caused much confusion concerning the fertilizing value of this compound".

Dr. G. H. Collings in his book "Commercial Fertilizer" (p. 189) states "phosphate rock carries fluorine in combination with tricalcium phosphate. As calcium and fluorine form an exceedingly stable combination, this may offer the real explanation for the difference in availability of apatite (phosphate rock) and Tricalcium phosphate."

In what form does phosphate exist in Superphosphate Fertilizer?

One of the purposes of acidulating phosphate rock is to disrupt the calcium fluor-phosphate combination. In superphosphate fertilizer the phosphate exists as water soluable monocalcium phosphate (Ca H_4 PO₄) soluable in a weak solution of citric acid and insoluable material. The mono and dicalcium phosphates are the available portions of superphosphate fertilizer.

What happens when reversion takes place in calcareous soils?

When superphosphate is supplied to soils containing calcium carbonate (lime) supposedly some of the mono-calcium phosphate reverts to di and tri-

calcium phosphate. The extent and speed of this reaction depends on the conditions of moisture, temperature, amount of free lime in the soil, etc., however, there is little doubt that this reversion does take place to a lessor or greater extent, depending on conditions existing.

We recently conducted a laboratory experiment to determine the extent and speed of reversion. 25 grams of ground limestone was mixed with an equal amount of superphosphate fertilizer. One sample was left in a dry mixed condition and another was wrapped in filter paper and kept moist. The results were as follows:

		Analysis of	Mixture
		When Mixed	After 2 weeks
	Water Sol. P	8%	7.5%
Dry Mixture	Citrate Sol. P	1.8%	2.3%
	Insoluable P	.2%	.2%
	Water Soluable P	8%	3.4%
Moist Mixture	Citrate Soluable P	. 1.8%	6.4%
	Insoluable P	.2%	.2%

This shows that in the dry mixture very little reversion took place the water soluable decreased .5% and the citrate soluable increased a corresponding amount. In the moist mixture 4.1% of the water soluable reverted to the citrate soluable. There was no change in the insoluable in either case. This would indicate that at least most of the reversion was from monocalcium to dicalcium phosphate.

It is then not so much a question of whether or not reversion takes place, but rather a question of the availability of the reverted product precipitated di and tricalcium phosphete.

Availability of Tricalcium Phosphate

Dr. Emil Truog of the University of Wisconsin, one of the outstanding authorities on phosphate fertilizer, stated to me, in a letter dated Dec. 18, 1946, "We do not worry about reversion of superphosphate because when the phosphate does revert and becomes precipitated as tricalcium phosphate, it is so finely divided that it is readily available. In fact, it is better to have it precipitated as tricalcium phosphate than have it combine with iron oxides and other constituents in the soil in which case it will be much less available than in the form of tricalcium phosphate. In fact, it may be said it is highly desirable that the phosphate in superphosphate be precipitated as tricalcium phosphate. That is one reason we tell our farmers to lime their soils up to PH 6.5. At that PH a large share of the phosphorus will be kept in the form of tricalcium phosphate and will be readily available."

Of course, we realize he is referring to acid soils and that tricalcium phosphate may be more available in these soils than in our intermountain soils which have a PH of 7 and higher.

However, as early as 1916 Truog grew various crops in pots of quartz send and fertilized them with various phosphates. The growth of crops with superphosphate were taken as normal and represented by 100. Under these conditions he found that tricalcium phosphate gave him a response of 99 on alfalfa.

Professor S. D. Conner of Purdue University stated that "even when mixed with limestone the availability of superphosphete as measured by crop response is not appreciably affected. He calls superphosphate a fool proof fertilizer and says it stays available for crops whether used directly or previously mixed with lime.

There is not a large amount of research information with regard to the availability of tricalcium phosphate in our intermountain basic soils. However, W. T. McGeorge of the Arizona Experiment Station has done considerable work on the subject for a number of years. In Arizona Technical Bulletin No. 82 he states that "soluable phosphate, fertilizers are fixed in a form which is surprisingly available as shown by the residual response obtained in pots and in the field" and he further states that "raw rock phosphate is of practically no value as a source of plant food phosphate on alkaline calcareous soils."

In a letter to me dated Jan. 21st, 1947, Mr. McGeorge states, "I believe that there is rapid fixation and reversion. This process is in the nature of a precipitation or dicalcium and tricalcium phosphate with possibly some anion adsorption of PO₄ by the soil colloids. In such forms I believe the phosphate remains available in the soil for an indefinite period. In one field experiment which I conducted where 600 lbs. of Treble Superphosphate was added per acre, there was a residual response for six years. I do not think that fixation or reversion seriously reduces the availability of superphosphate unless it goes clear over to a carbonate phosphate (CA₃ (PO₄)₂ Ca Co₃). I think the unavailable phosphate in calcareous soils is present in this form, but we do not know the conditions under which the carbonate - phosphate is formed."

Why is reverted Tricalcium Phosphate likely to be available to a large extent in calcareous soils.

Jesse Green of the Anaconda Company states, "We think of triphosphate as a very insoluable compound and this is true in pure water solutions, but conditions are different in soil. There the plants send out tiny rootlets which give off carbon dioxide with the ability to redissolve insoluable phosphates. If this were not the case no plants could live; also, if phosphates were not more or less insoluable, they would be lost too rapidly from the soil. The insoluability of phosphores and the ability of plants to redissolve them shows a wonderful design in nature."

Vincent Sanchelli of the Davidson Chemical Corporation, states, "In the process of reversion an extremely fine state of division is obtained. He points out that Eock phosphate ground fine enough to pass through a 100 mesh sieve has a particle diameter of 148000 millimicrons while colloidal phosphate has percipitated in the soil from superphosphate has a diameter of 500 to 50 millimicrons. This gives a relative surface area of 1100 to 11000 for precipitated colloidal phosphate as compared to 1 for 100 mesh rock phosphate.

Collings in his book "Commercial Fertilizers" P. 189, also refers to the thorough dissemination of the micro sized particles of precipitated tricalcium phosphate. However, he indicates that more important is the fact that the exceedingly stable calcium fluoride complex of the phosphate rock is broken up by acidulation and this complex is not formed again when superphosphate reverts in the soil.

There then appears to be three reasons why the precipitated tricalcium phosphate formed by reversion of superphosphate is available or becomes available for plant use.

- 1. The soluability of this material in weak carbonic and organic acids formed in the soil.
- 2. The fine state of division and thorough dissemination of this material in the soil which exposes more surface area to the plant roots.
- 3. The fact that the calcium fluorine combination is broken up in the manufacture of superphosphate and is not formed again in the soil.

Evidence of the availability of reverted phosphate in the soil.

The best evidence that reverted phosphate is not a loss, but rather becomes available for plant use, is in the residual effects obtained from superphosphate. This effect is known to all soil scientists, Agronomists and others who have worked with phosphate fertilizers in the field, to the extent that it is accepted as common indisputable knowledge. This fact is also known and recognized by the farm users of superphosphate.

Jesse Green of the Anaconda Company recognizes residual effects from one normal application will last up to three years. I have already quoted Mr. McGeorge of the Arizona Station as stating he obtained residual effects up to 6 years. Practically all other Experiment Stations can report similar results.

In the spring of 1945 I established a number of trial plots with superphosphate in the upper Snake River Valley of Idaho. Single Superphosphate was applied at the rate of 400 lbs. per acre. In 1945 the average hay yield from all of these fertilized plots was 4.4 tons as compared to 2.2 tons for the unfertilized plots. These plots were again checked in 1946 and produced an average hay yield of 4.2 tons as compared to 2.4 tons for the unfertilized plots. This is a total increase in two years of 4 tons of hay. We assume that the natural phosphate supply of the soil was furnishing only enough phosphorus to produce the yield obtained on the check plots. Then the extra 4 tons was produced from the phosphate fertilizer added. This 4 tons would remove about 60 lbs. of phosphorus, 72 lbs., were applied. Therefore, very little, if any, loss occurred. I am certain the remaining 12 lbs., will show up this year. Their soils are highly calcareous. We are reasonably certain reversion took place and the results indicate the reverted phosphate was available. The increased root development resulting from superphosphate, may make it possible for the plant to break down more of the natural phosphate in the soil.

Recent work and Opinions on the practical aspects of this problem.

The practical aspects of this problem with regard to use of superphosphate involve the time of application, the rate of application, the method of placement or application, the use of superphosphate with menure, and the economics of using phosphate fertilizers.

With regard to the time of application, it was formerly generally recommended that phosphate fertilizer be applied as near to the plant growing period as possible to avoid as much loss from reversion as possible. This worked a hardship on the fertilizer industry by expecting them to supply a years demand of fertilizer in a short period in the spring. It also worked a hardship on the farmer who is extremely busy in the spring. It is generally conceded now, however, that superphosphate is a year around fertilizer and can be successfully and economically applied in the fall or any time of the year, especially on hays and pastures. I have correspondence from the Idaho, Oregon, Washington, Montana, and Arizona Experiment Stations recognizing the value of and approving fall application of superphosphate.

John L. Toevs, former Superintendent of the Aberdeen, Idaho branch Experiment Station, advised me that his work indicates that superphosphate can be applied any time of the year, with equal results over a period of time. He stated, "it doesn't matter so much when and how you apply it - the main idea is to get it on the soil."

In the fall of 1945, I established 5 trial plots with superphosphate on alfalfa in Eastern Ideho in 4 different counties. I again duplicated these trials in the spring of 1946. The average yield of these 5 trials was 5.1 tons hay from fall application and 4.8 tons from spring application a difference of .3 ton in favor of fall application. This .3 ton of hay @ \$15.00 per ton would pay for two thirds the cost of the fertilizer. The difference in every case came on the first cutting of hay. Numerous farmers are using superphosphate in the fall and have testified to the value and advantage of this practice.

The method of application is influenced primerily by the type of equipment available and the type of crop grown. It is generally conceded advantageous to get the fertilizer in the soil and close to the plant. This is especially true for row crops. On hay and pesture, broadcasting is about the only practical method of application and seems to give the results regardless of the statements made against this practice. Plow sole application or broadcast and plow under may prove valuable where applicable. It is generally believed that placing the fertilizer in the soil in bends is the most efficient method from the standpoint of returns.

The amount of reversion and the availability of the reverted phosphate has a definite bearing on the rate per acre. Generally heavier rates per acre return more per dollar invested in fertilizer up to a certain amount, which is usually beyond the rate the average user applies superphosphate. It is considered better to apply a heavy application every other year, than a light one every year. This holds true especially on alfalfa. We have found that in Idaho somewhere between 400 to 600 lbs., of single superphosphate or 80 to 120 lbs., of available P_2O_5 seems to give the most economic returns.

The results and returns from both method of application and rate per acre depend on whether you base your returns on one crop or on a rotation

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period. The latter is a more accurate measure and tends to level out variances obtained from different methods and rates based on one crop.

Use of Superphosphate with manure.

The use of superphosphate with manure is of interest to all sugar beet growers since the manure is usually applied to the beet land. This practice is also directly related to the subject of reversion since when superphosphate is applied to manure supposedly about the same reaction occurs as when it is applied to calcareous soils. The ammonia in the manure combines with the phosphate to form ammonium phosphate, and with the gypsum in single superphosphate to form ammonium sulphate. Calcium is released, which in turn combines with carbonates in the manure to form calcium carbonate (lime). This calcium carbonate is then assumed to tie up or revert some of the monocalcium phosphate. However, if precipitated tricalcium phosphate is available in the soil, this is of no concern.

The use of superphosphate as a reinforcement for manure has been practiced successfully for many years and highly recommended by eminent authorities. Even those who have questioned the practice have recognized its many merits and questioned it with reservation. In the 1938 year book "Soils and Men", page #456, the data of Midgeley of Vermont, is interpreted by Salter and Schollenberger of Ohio, as follows, "one ton of 20% superphosphate costing \$23.50 in 1937 should fix 140 lbs., of ammonia nitrogen work \$12.00. In the process, however, all of the available phosphoric acid of the superphosphate is changed to the insoluable tricalcium phosphate."

This early work apparently did not hold under practical use of the practice. The use of phosphate with manure has gained in popularity every year and many farmers have testified to the value of this practice. I have seen a number field trials which did not support these theories of loss. In Chemurgic Papers No. 1, 1946 series, published by the Chemurgy Digest, A. R. Midgeley of Vermont Experiment Station apparently reversed his earlier thinking on the subject or at least that of interpreters of his data. In an article entitled use of sawdust, shavings and superphosphate with Dairy Manure" he stated:

"Superphosphate has long been used as an amendment to cattle manure. It makes the manure a better balanced fertilizer by supplying phosphoric acid and, when properly used, it helps save some ammoniacal nitrogen which would otherwise be lost into the air.

The use of superphosphate in the dairy stable gutter, together with adequate bedding, greatly increases the fertilizing value of manurc. To be most effective, superphosphate should be added in the bottom of the cleaned gutter where the urine dissolves and ammoniates the superphosphate (Literature note 2). While the 20% grade of superphosphate can hold over 7% of its weight in ammonia when completely ammoniated commercially, it seldom holds more than half this amount when used with manure. This is due to the highly viscous nature of manure, its low ammonia content, and the fact that most of the ammonia in the manure is present as the carbonate rather than the hydroxide form. Nevertherless, much nitrogen can be saved by the use of adequate bedding and superphosphate. This is shown in Table 2.

Some of the samples were fermented for a week and sir-dried, in order to study the virtue of the added amendments. The results of the experiment show that all the bedding materials tested help to save some nitrogen. However, the losses were very large. This is due to the fact that the manure was air-dried before analyses were made. When this is done, even the bedding fails to hold much water and the dissolved ammonia evaporates with it. However, when superphosphate was used with bedding, substantial savings of nitrogen were obtained even though the materials were air-dried, as is often the case under farm conditions.

Manure has a beneficial effect on the availability of phosphate applied to high phosphorus fixing soils. Phosphated manure has been found to produce considerably better crop growth than the same amount of superphosphate and manure applied. separately (Literature note 1). This superior crop growth, due to increased availability of phosphate, is in addition to the value of superphosphate in holding nitrogen. One reason manure reduces phosphate fixation in soils is that the phosphate goes with the manure, and soil contact is reduced. Since each piece of manure contains some phosphate, it tends to become "pelleted" and concentrated within the soil. This reduced soil contact reduces fixation. Furthermore, when superphosphate is added to manure, its immediate solubility is reduced, as a result of the formation of some hydrated, tricalcium phosphate. This reduced solubility is a blessing in disguise because it lessens reaction with the soil, but the phosphorus still remains available to plants. Freshly precipitated, hydrated, tricalcium phosphate has been found to be a good source of available phosphorus for plants especially in the presence of actively decaying organic material such as manure."

I have correspondence from a number of the western Experiment Stations wherein they recognize the value of the use of superphosphate as a reinforcement for manure and recommend the practice.

Jesse Green's work in Montana has shown this to be a good practice. A.A.A. in many states makes a payment for it. I feel that altogether the recent evidence is very favorable on this practice and it should be encouraged.

CONCLUSIONS

Based on the evidence available at the present time, it appears safe to assume that the tricalcium phosphate formed in calcareous soils by reversion of superphosphate is largely available or becomes available for plant use.

Regardless of whether or not reversion takes place and the availability of the reverted product is questioned, we need superphosphate, we will continue to use it, and its use will prove economically sound and profitable. Therefore, the question of reversion should not concern us near as much as our responsibility to encourage and assist the farmers to do a good job of farming. We cannot do much about reversion, but through encouragement of proper rotation of crops, the use of manure and green manures, and other practices that build up organic matter, we can accomplish a great deal to overcome fertility losses whether they be through fertilizer reversion or other losses.

Calcium reversion is the least undesirable form of reversion. Our neighbors to the east have Iron and Aluminum fixation to concern them. They also have to lime their soils and are apparently glad to get calcium reversion as a desirable means of holding the phosphate in their soils. On a total of 19 trials, in 9 counties, in Eastern Idaho which I conducted in 1945 and 1946 with superphosphate on alfalfa, the average increase was 2.6 tons hay for a net profit of \$34.00 per acre. The 1945 trials gave a residual effect in 1946 which practically doubled this profit. The 1946 trials will do likewise in 1947. In addition the use of superphosphate raised the phosphorus content of the hay .06% and the protein content 2%. These farmers are not concerned about reversion of superphosphate, it has already paid them \$5.00 for every \$1.00 invested. The Aberdeen Branch Experiment Station at Aberdeen, Idaho, has reported a net profit of \$181.00 per scre over a 6 year rotation period with the use of phosphate fertilizer.

Dr. Albrecht of the University of Missouri reports, "it takes the dumb animals to convince us of the lasting effects of fertilizer." He cites a case where cattle showed preference for hay from a field as long as 8 years after it was fertilized.

We are at present supporting a followship at the University of Idaho for research on the reversion of superphosphate in colcareous soils and we hope to have some definite information to report to you at your next meeting.

Production of low yields and poor quality is due more often to a lack of phosphorus than to the lack of any other element - Superphosphete has aptly been called "the master key to agricultural prosperity."