Technical Management. December 2013
Rev.3

INDEX

AGRONOMIC APPLICATION OF PHOSPHATE ROCKS

1. IMPORTANCE OF PHOSPHORUS IN NUTRITION

Phosphorus takes part of important organic compounds such as glucose, nucleic acids, some coenzymes and phospholipids. It stands out mainly for being a component of the adenosine triphosphate ATP of great importance in plant metabolism due to its role in the storage and transport of the energy produced in photosynthesis and respiration processes that, once released, is used in the absorption of nutrients and in the synthesis of sugars.

At the physiological level, phosphorus works primarily on the root development, favouring the root cells proliferation, with an increase of absorbent hairs. Also affects the flowering mechanisms, pollen tube development, pollen germination, pollination and fruit setting.

Given the important metabolic and nutritional functions which phosphorus plays, the plant extract it on important quantities, becoming with nitrogen and potassium, essential macronutrients in fertilization.

Its deficiency firstly appears in older leaves, being the lower ones most affected arriving to dry out, even if deficiency affects the whole plant. It takes a characteristic green dark purple appearance, with yellow lower leaves that turn a greenish-brown. The vegetative development is clearly affected, especially the lateral growth and the very low final production.

2. MOVEMENT OF PHOSPHORUS IN SOIL

Phosphorus in the soil can be found in the organic or inorganic form. The amount of organic phosphorus in the soil can reach 500 Kg / ha. in podsols, while in chernozium can reach up to 1500 Kg / ha. The most frequent form is the phytin formed when phosphoric acid works over inositol and calcium and magnesium salts, forming inositol hexaphosphate. Depending on the soil, the phytin constitutes between 30 and 80% of the whole reservation of the soil organic phosphorus. Nucleic acids are also an important source of phosphorus, representing 10%. Lecithins and phosphoproteins are other forms of organic phosphorus.

Part of the phytin can be assimilated directly by plants or after ferments, caused by root secretions, have worked; but an important part is degraded by the soil microorganisms into inassimilable ways.

The organic phosphorus movement in soil is very low as consequence of fixing that occurs with different organic and mineral materials, so if it is in far stratus of root masses, affects sparsely in nutrition of crops.

Regarding inorganic phosphorus, they are in the orthophosphates or natural phosphates forms, normally of very low solubility, so they are characterized also by their insufficient movement in soils and its low assimilation by crops, being susceptible to the same way of fixations and immobilizations in soil. However they are the main source of phosphate supply for crops and how that provides phosphorus by means of fertilizers.

3. FIXATION OF PHOSPHORUS IN SOIL. ASSIMILATION FORMS.

The fixation of phosphorus in soil occurs by iron and aluminium oxides, clay minerals and calcium bases. In acid medium occurs fixation by iron and aluminium oxides, being absorbed on its surface and forming the corresponding phosphates, while in an alkaline or neutral medium, phosphates are fixed on calcite by means of calcium ions replacing water molecules, bicarbonate and hydroxyls, and low solubility and low assimilation tricalcium phosphates are formed. Also with magnesium in alkaline or neutral conditions, takes place a formation of magnesium phosphates which are also characterized by their low solubility and assimilation.

Plants absorb phosphorus in the form of dibasic phosphate ion $HPO_4^{=}$ or monobasic $H_2PO_4^-$, being slowly assimilated. In cation exchange complex of soil, phosphates mainly are adsorbed by means of bridges of calcium, magnesium and iron and are gradually transferred to the soil solution which are absorbed by root hairs. Phosphate adsorbed on the clay-humic complex becomes increasingly slower replaceable by other ions, and the fraction of exchangeable phosphorus decreases.

Other important fixation occurs thanks to the humus reactive groups of soil, especially fulvic acids, forming complexes with phosphorus through calcium bridges, humo-phosphates or rather fulvo-phosphates, since they occur primarily thanks to carboxylic groups of lateral aliphatic chains of fulvic acids, which are acid and allow to attack insoluble salts, specifically phosphorus salts mentioned above. These compounds are easily assimilated by plants. They may also be formed by means of iron and aluminium bridges, although to a lesser extent, forming inorganic orthophosphates. Humic substances work into a protective way in relation to soluble phosphates precipitation and they have a solvent action on insoluble phosphates, in such a way that fulvic-phosphates are actively involved in the phosphate nutrition of plants.

The capacity of phosphorus absorption by roots decreases to low temperatures and extreme pH. Also is influenced by the specific capacity of roots, variable according to crops.

In one way or another, phosphorus even in significant quantities in soil, in general a considerable proportion is found in inassimilable forms.

Precisely the manufacture of phosphate fertilizers consist of transforming natural phosphates in higher solubility products, that is, of greater assimilation by plants. However passing to the soil, can occur fixations and immobilizations, in such a way that fertilizer efficiency may be frequently diminished.

4. PHOSPHATE FERTILIZERS

As mentioned, the manufacture of phosphate fertilizers consist basically of transforming natural phosphates into higher solubility products and therefore of greater assimilation. When natural phosphates suffer the attack of sulphuric acid we obtain superphosphates. And attacking them with phosphoric acid, we get triple superphosphates and typical phosphoric acid. With a partial phosphoric acid neutralization together with ammonia, the result is monoammonium phosphate, and with a more intense neutralization, diammonium phosphate. All these fertilizers differ in their phosphorus solubility, in such a way that their assimilation is directly connected to their solubility.

Fertilizers normally used in agriculture are therefore simple superphosphates (SSP), triple superphosphates (TSP) and ammonium phosphates (mono and diammonium), and in lower proportion natural phosphates, phosphate rock or phosphorites.

However when phosphate fertilizers are incorporated within the soil, always they may occur phenomenons of fixation, blocking or precipitation as above mentioned. The reaction with soil materials originates a characteristic scarce movement of phosphorus and its reversion into insoluble forms or of low solubility.

The most frequent reaction occurs with limestone soils, characterized by a slightly alkaline pH, where phosphates applied to soil precipitate into difficult solubility forms. Phosphorus evolves slowly and irreversibly into unrecoverable forms for crops nutrition, specifically calcium phosphates. This occurs as a result of the reaction with calcium hydroxide or carbonate, forming dicalcium or tricalcium phosphate, that quickly becomes hydroxyapatite and then fluorapatite in the fluorides presence (frequent in superphosphates), of very low solubility. Thus tricalcium phosphates are ineffective and soluble are fixed into slow assimilation forms, depending on soil humidity, temperature, and reactivity.

Highly acid soils ($pH < 4$) and rich in iron and aluminium, also they may form insoluble phosphates, but this reaction becomes reversible slightly neutralizing with lime amendments. Slightly acid medium (pH 4-6), on the other hand, maintain the highest proportion of soluble phosphates, mainly as monocalcium phosphates.

Consequently, we always find that with the application of any phosphate fertilizer, they may occur fixation, blocking or immobilization in soil, in such a way that it may reduce its effectiveness.

We know that with time, and with the action of soil microorganisms, and the light excreted ferments acidification in rhizosphere, there occur conditions where phosphorus is reverted partially into soluble forms, although it is only a gradual and phased action.

5. PERFORMANCE OF NATURAL PHOSPHATES IN SOIL

Natural phosphates as above mentioned, are used as raw material for superphosphates and ammonium phosphates production, with higher solubility and therefore, higher crops assimilation.

However, natural phosphates may be used directly without any transformation in conditions that favour their dissolution in soil as in acid soils that dominate in large geographic areas of the world. A low concentration of calcium ions in solution, a low level of phosphorus fertility and a high organic matter content, also favour the dissolution of phosphate rocks.

Phosphates are primarily apatites of carbonate-fluorapatite type, known as francolites, mostly of sedimentary origin (80-90% of sites), and the rest of igneous origin.

Generally, when applied to the soil, occurs the following reaction:

$$Ca_{10}(PO_4)6F_2 + 12H_2O \longrightarrow 10\ Ca^{2+} + 6H_2PO^{4-} + 2F^{-} + 12OH^{-}$$

The dissolution of phosphate rock, generates hydroxyl ions in the soil solution and these ions neutralization by the soil acidity, allows that the dissolution continues. In phosphate rocks, part of the phosphate ions are replaced by carbonate ions, and therefore there are needed also hydrogen ions to neutralize hydroxyl ions formed during the carbonate ion relase in solution. It is therefore necessary the hydrogen ions supply produced in acid soils, for a good phosphate rock dissolution and a good crop assimilation.

Calcium ion in soil solution should be decreased for favouring dissolution conditions of the rock, by means of its fixation in the soil cation exchange positions or leaching out of the reach of roots.

Soils with higher cation exchange capacity, higher nutrient retention capacity, favour the phosphate rock dissolution to retain calcium which will decrease in soil solution. Therefore in soils with greater CEC the agronomic action of phosphates will be better. Consequently, the soil texture affects the agronomic action, favouring it in clay and loam-clay soils.

Rainfall or irrigation, can favour the calcium leaching in the soil solution and therefore they will facilitate the rock dissolution. It also favours a rapid neutralization of released hydroxyl ions by moving them from the area of rock, making easier its dissolution. Normally we talk about rainfall greater than 850 mm. For a phosphate rock agronomic efficiency similar to water-soluble phosphates, depending on soils. Other cations such as magnesium, also favour its action, to compete with calcium, since it is retained by the soil more strongly than this and it can block the adsorption of the calcium released from the rock dissolution, lost by leaching.

Regarding the retention capacity of phosphorus in soil, if bigger, there is a phosphorus decrease in the solution close to the phosphate, and an increase in the phosphate rock efficiency to favour the phosphorus release from this. When reduced doses of phosphate are applied to soils deficient in phosphorus, is strongly adsorbed phosphorus in the soil, leaving a small amount in the solution, so the efficiency of cultivation does not increase much. That is, for soils of medium to high fertility in phosphorus, it is enough a maintenance dose (same amount extracted by crops) for obtaining immediate results from the rock application. Available phosphorus for crops helps the root development making easier the efficiency of the phosphate use. It should be expected that phosphorus released by rock must be at least the same to the extracted by crops plus the retained by soils in an unavailable form.

Regarding the organic matter, as we know it is characterized by its high cation exchange capacity (up to 200 cmol/kg opposite to 60 cmol/kg.of clay soils), the formation of complex organic-calcium matter (carboxylates) and the presence of organic acids which block the retention sites of phosphorus in soil. High CEC and the formation of carboxylate complex increase the calcium retention capacity and therefore a higher rock dissolution. Organic acids dissolve phosphate rock to provide hydrogen ions that neutralize hydroxyls favoring their action, in addition to form calcium complexes. Soil phosphorus retention capacity is reduced to block the phosphorus adsorption sites and form iron and aluminium complexes, increasing phosphorus concentration in the soil solution, and therefore the rock action.

Depending on the present crops, also it is produced a better use of phosphates, for example in permanent pasture especially legumes and tree species and perennial plantations that require a phosphorus supply for a prolonged period. Extensive root developments that explore large amounts of phosphorus, favour the rock action, while legumes require calcium and they acidify to fix atmospheric nitrogen.

6. INFLUENCE OF PHOSPHATE ROCKS OVER THE ALUMINIUM TOXICITY IN ACID SOILS.

Another important aspect to consider when rock phosphates are applied in acid soils, is the possible toxicity caused by iron and aluminium in crops.

Acid soils are widely distributed in tropics. More than 50%, that is, 2600 million hectares, are considered acid ($pH<5.5$). Almost a third of all tropical soils, 1500 million hectares, have a soil acidity that is strong enough for the aluminium becomes toxic to most of the cultivated species. Most of these soils are in humid tropics and acid savannahs , even though there are some soils in the rugged tropical lowlands.

Soils in semi-arid tropics and tropical wetlands do not tend to have this problem. Aluminium toxicity is usually found in soils called Oxisols, Ultisols, and Distropepts, which tend to be enough weathered soils, low in organic matter and with few reserves of nutrients.

When soil pH is 5.5 or more, aluminium is strongly associated with insoluble inorganic matter, and therefore it can't be absorbed by plant roots, being in the form of unavailable precipitates hydroxides. If pH is less than 5.5, and especially less than 4-5, an increasing proportion of total aluminium present in soils is found in the soil solution or weakly associated with clay and organic matter. This ion form, Al^{3+} is bioavailable (it can be absorbed by the plants roots) and in this way it may be harmful for the growth of plants.

There are two main ways in which bioavailable aluminium (Al^{3+}) can have a negative impact on the plant growth: it may interfere with the plant absorption by essential calcium nutrients (Ca) and magnesium (Mg), and it can be directly toxic for roots.

Aluminium Al^{3+} can compete with these ions for the absorption, causing deficiencies in Ca and/or Mg in plants. These deficiencies would not occur if Al^{3+} concentrations were lower. Al^{3+} can also causes deficiencies of Ca and/or Mg to increase the amount of Ca^{2+} and Mg^{2+} leached from the soil.

When aluminium is dissolved in a low pH, soil has a less retention capacity of Ca^{2+} and Mg^{2+}, so that ions of these nutrients have a higher tendency to leach themselves from the soil. When Al^{3+} concentrations in the soil water increase as result of low pH conditions, Al^{3+} will compete with Ca^{2+} and Mg^{2+} for binding sites, resulting in a higher leaching of these soil ions. In addition, regardless of the Al^{3+}concentration, the ability of a plant to build essential ions such as Ca^{2+} and Mg^{2+} is less when soil pH is less than 5, than when there is a more neutral pH (6-7).

Bioavailable aluminium form also can be toxic to the plant roots. The mechanism by which this happens is still not well understood, but it seems that the highest damage occurs at the roots tips. Al^{3+} reduces both the root cellular division as its growth, resulting in short and thick roots. This in turn reduces the roots capacity for providing water and the necessary nutrients to the plant.

Toxicity caused by aluminium reduces the depth of roots, increases susceptibility to drought and decreases the use of nutrients from subsoil. Aluminium affects the elongation of roots reducing mitotic activity. Roots damaged by aluminium are short and brittle, radical apices and lateral roots increase and acquire a brown coloration. Roots affected by aluminium are inefficient in the water absorption and nutrients. In general, young seedlings are more susceptible to aluminium than old plants.

Phosphorus deficiencies may be more pronounced when root system of plants is inhibited, due to their scarce mobility. On the other hand Al^{3+} reacts with phosphorus in the soil solution, making it less available to the plant roots.

Thus, the effect of the aluminium toxicity is mainly caused by nutrients deficiencies (such as Ca and Mg) or a root elongation inhibition.

Symptoms of the aluminium toxicity are not easily identified, since they may be confused with P deficiencies (dwarfism, small dark green leaves, late-maturing; stem-redness, leaves and nervations, yellowing and leaf apices death). In other plants the aluminium toxicity appears as an induced Ca deficiency or as a reduction problems of Ca transportation (making room for ruffling or curling in young leaves and apices collapse or petioles).

It has been suggested that the aluminium toxicity begins at the sites of synthesis of polysaccharides. Aluminium ions join themselves very specifically to mucilage by absorption exchange of polyuronic acids, forming complexes with pectic substances and by polyhydroxilics forms formation, increasing the number of aluminium atoms by positive charges. The aluminium is adsorbed onto sites that bind to calcium in the cell surface.

Usually the different species of plants (or cultivars within species) differ in their ability to tolerate stress due to the presence of aluminium. Plants possess mechanisms of resistance to tolerate aluminium, such as reduction of lesions on roots, increase of soil pH near the root surface (so Al^{3+} precipitates and becomes less bioavailable), organic acids secretion to form complexes with Al^{3+} (less bioavailable), less transport of aluminium at the top of plants, higher capacity for accumulating Ca^{2+} and/or Mg^{2+} despite the presence of Al^{3+}, etc.

The application of rock phosphate to soil, reduces the aluminium toxicity, given that it is toxic for plants only when it is soluble and aluminium solubility greatly dependens on the soil pH. As the pH increases less than 4-5 up to between 5.5 and 6, Al^{3+} is precipitated out of the soil solution and will no longer be bioavailable to the roots of plant.

The reactive phosphate rocks or phosphate rocks containing free carbonates (calcite and dolomite) can contribute to increase the soil pH for partially reducing the aluminium saturation in acid soils and reducing the aluminium toxicity of aluminium for the growth of plants.

The application of phosphate rocks of medium to high reactivity in tropical acid soils highly formed has a potential effect of «start» over the plant growth and the yield of crops, as a result not only of the phosphorus sypply but also of the increase in exchangeable calcium and the reduction in aluminium saturation.

A research done by the International Center for Soil Fertility and Agricultural Development (IFDC) has shown that the the phosphate rocks application with medium-high reactivity and with low free carbonates may have as a result important effects of liming on acid soils. While the increase in pH is usually less than 0.5 units, the reduction of exchangeable aluminium can be significant when soil pH is less than 5.5 considering that in oxisols and ultisols the exchangeable aluminium level would be almost nil in this pH to apply phosphate rock (Pearson, 1975).

The application of rock phosphates decreases the exchangeable aluminium up to 75% (up to 4 cmol/Kg), while increases the exchangeable calcium up to a 800% (several cmol/kg), according to a study published by the University of Malaysia (Cristancho, J.A. et al. 2009) for the acid soils of Malaysia.

7. PHOSPHATE ROCKS REACTIVITY

Reactivity, is defined as a measure of the dissolution rate of rocks under standard laboratory conditions or in a given soil and under certain conditions of field. To further dissolution, greater agronomic efficiency.

The chemical composition and the rocks origin as well as the size of particles, condition reactivity.

The crystal structure of phosphate and the carbonate presence, influence the reactivity, in such a way that in rocks of sedimentary origin with smaller crystals, higher specific area, higher porosity and less consolidated structures, reactivity is greater than the in rocks of igneous origin with more compact and large crystals.

The level of carbonate substitution into apatite, increases the reactivity by the weakening of the crystal structure, such that the most reactive have a PO_4/CO_3 molar relation of 3,5-5 or a CaO/P_2O_5 relation of at least 1.6. When the level of the isomorphic substitution of PO_4 for $\mathbf{CO_3}$ is higher in the structure of the apatite CO_3/PO_4 (on the order of 0.2), solubility will be higher in reactive standards.

Carbonate linked to the crystalline apatite structure is what determines the solubility of phosphate rock, total carbonate, calcite, dolomite or free carbonates. In fact, as calcium carbonate is more soluble than phosphate minerals of higher chemical reactivity, its dissolution increases calcium concentration and pH on the phosphate mineral surface, and it could reduce the rock solubility, but in conditions of field, leaching and phosphorus absorption by crops can remove calcium. If rock contains more than 15% of free calcium carbonate, it can decrease their agronomic effectiveness in high pH soils, but on acid soils, the replacement of calcium phosphate for apatite, increases the rock reactivity.

Moreover, the calcium from the rock in an acid medium, is an essential nutrient for crops that often are lacking in these conditions. However if solubilization of free carbonates significantly increases the pH and exchangeable calcium around the particles of rock, the availability of phosphorus from rock can be reduced.

The other factor that affects rocks reactivity is the size of particles. Since the phosphate rocks are relatively insoluble, the particle size has an important effect on the dissolution rate of themselves. More finesse, more contact between phosphate and soil and therefore higher dissolution. In addition, the increase of the particles number per unit/weight of the applied rock, increases the root absorption and therefore, the efficiency. Below 0.15 mm. it favours the dissolution rate of rock, that is, its reactivity. However if reactivity is low, the very fine grinding may not increase its solubility significantly if there is a low substitution of PO_4 for CO_3 in the apatite structure. If reactivity is high, solubility increases, but agronomic performance is similar, so it is not necessary to finely grind the highly reactive phosphate rocks for direct application.

Reactivity can be measured in laboratory in several ways, but mainly, phosphorus is extracted by means of solutions of weak acids that simulate root exudates conditions in the rhizosphere area and is therefore an approximation of assimilable phosphorus for crops, in such a way that it can be used as means of extraction, the neutral ammonium citrate, 2% citric acid or 2% formic acid. The phosphorus proportion that has been extracted from these means with respect to the total, gives us an idea of the rock reactivity. More phosphorus extracted, higher agronomic efficiency.

The level of chemical extractability that rocks need to be agronomically effective, depends on soil and weather-rain conditions. In very acid soils is often recommended at least 20-30% of phosphorus, soluble in 2% citric acid, but in not much acid and neutral soils it is advisable at least 40-50% soluble in 2% formic acid. However, they sometimes have a low level of extractability and however have a good agronomic efficiency as result of iron sulphide oxidation present in the apatite to sulphuric acid and to the localized acidulation of phosphate rock and due to its content in organic carbon that improves the internal porosity and its own dissolution..

Formic acid solubilities are normally higher than the citric acid, while in neutral ammonium citrate there are smaller amounts, and often a second extraction is needed for eliminating the interference of carbonates and so obtaining more real results. Carbonates interfere less on extraction acid elements, so the 2% formic acid is preferred as a simple extraction chemical method because it is the stronghest among weak acids.

There is not a simple and accepted system for classifying phosphate rocks, but in an orientative way, may be taken into account the following table carried out by Diamond. R.B. (1979):

Rocks classification according to the solubility and the expected first response

Phosphate rock potential	Solubility (% P_2O_5)		
	Neutral ammonium citrate	Citric acid 2 %	Formic acid 2 %
High	> 5,5	> 9,4	> 13
Medium	3,2-4,5	6,7-8,4	7-10,8
Low	< 2,7	< 6	< 5,8

Some phosphate rocks are completely hard to solubilize due to they are cemented by silica, but it is not usually a condition of phosphate rock reactivity.

8. AGRONOMIC EFFICACY COMPARED TO SOLUBLE PHOSPHATES

Several studies show that in acid soil conditions, the agronomic performance of phosphate rock may be similar to superphosphates.

In conclusion, as discussed in previous section, the factors affecting on the agronomic efficiency of phosphate rocks belong in addition to reactivity, soil characteristics, climatic conditions, cultivated species and crop management practices. A high substitution of phosphate for carbonate in the apatite crystal structure, a low calcium carbonate content as mineral accessory and fine particle size (< 0,15 mm), increase the rock reactivity and its agronomic effectiveness. The increase in the acidity of soil, a high cation exchange capacity, low levels of calcium and phosphate in the solution, a high rainfall or irrigation and a high organic matter content, favour solubilization and agronomic action of phosphate rocks.

In tests carried out in a greenhouse, they have the advantage to control soil and climate conditions, which allow obtaining conclusions about the suitability of direct applications of phosphate rock through gramineae and other short-cycle plants cultivation using application doses of 25-400 mgr. of phosphorus /kg. soil, although low doses up to 50 mg/kg may be insufficient in soils with few reserves and high phosphorus retention capacity.

In particular, experiments with several phosphate rocks (Truong et al.1978) and three types of acid soils (alfisol with low phosphorus retention capacity, vertisol with medium capacity and andosol with high capacity), gave better Agrostis yields for triple superphosphate than for rocks. However, these trials showed that in the three types of soil, the rocks reactivity, determines its agronomic potential value, being more sensitive to differentiate phosphate rocks, phosphorus absorption by the plant than the dry matter produced. This tendency is of great value because there is a direct correlation between reactivity and phosphorus and yields extraction by crops.

The index of relative agronomic efficiency (EAR) is used in some occasions as a percentage of the relation between the phosphate rock response and the soluble phosphate. The difference between both responses must be significant. We can calculate coefficients based on EAR for crop yield or dry matter production, phosphorus absorption, chemical extraction or labile phosphorus values. In the study performed by Truong et. al.1978, phosphorus absorbed by plants in andosol where was applied a high reactivity rock, obtained an EAR efficiency of 98% with respect to the triple superphosphate, while the other two soils, maintained 40-50% of EAR. Where applied a low reactivity rock, in andosol, was obtained an EAR of 42%. That is, the phosphate rocks classification for direct application remains relatively constant, but efficiency must be considered according to the soil properties. Under the described conditions, a high reactivity phosphate rock has an agronomic performance similar to a soluble phosphate as triple superphosphate.

Another qualification is that phosphate rocks are of relative slow solubilization, therefore time and water are needed to achieve their maximum agronomic efficiency, while there is a low concentration of phosphorus in the soil solution. The more reactive rocks were rapidly solubilized and their efficiency scarcely changed in four months, while less reactive rocks needed time to show its potential efficiency. The amount of water also influences the solubilization, especially for less reactive rocks.

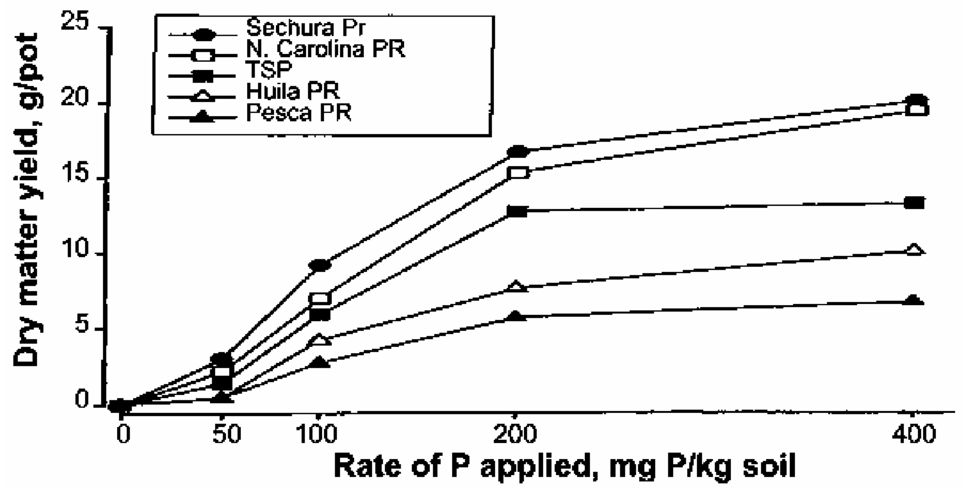
Generally, an increase in the rock solubilization should lead to an increase in available phosphorus on plants with an increase of the absorption and yield, but should be validated with field trials. The correlation coefficients were high for andosol and vertisol, but low for alfisol which pH was almost neutral (6.5), not being suitable for the rock solubilization.

In a study performed by Frederick et to the. 1992 and Lompo et al.1995, in Burkina Faso, in field trials, was used very low reactivity phosphate rock in millet, sorghum, maize and rice crops, reaching EAR yields of 80% in rice, 77% in corn and more than 50% in millet and sorghum. If acidulated with sulphuric acid (50%), the EAR reach was of 108% in rice (more agronomic effectiveness than TSP) and 70% in other crops.

It is interesting, a study performed by Chien, S.H. 1982 who employed high reactivity phosphate rocks and others of low reactivity in acid oxisol that he cultivated with Panicum maximum and compared with triple superphosphate. Several doses were applied from 50 to 400 mg.P/kg. of soil. The production of dry matter when high reactivity rocks were applied was significantly superior to triple superphosphate as you can see in the following graphic.

The best performance of rocks opposite the TSP, may be connected to this case with the decrease in aluminium toxicity, to have an specific effect of liming, as it became clear that the interchangeable fell from 2 to 0,4 meq/100 gr., the pH went from 4.6 to 5 and exchangeable calcium from 0.2 to 1.5 meq/100 g. The saturation level of aluminium decreased from 80 to 20 %

Effect pf P sources on *Panicum maximum* dry-matter yield (sum of three cuts) on an Oxisol



In tests performed by Truong et.al.1982 with phosphate rocks in Barren Islands (Madagascar), with acidic andosol (pH 4.3) and doses of 100 mg P/kg. and Agrostis sp. culture, phosphorus availability was higher with respect to TSP, so it was concluded that the phosphate rocks employed, are equivalent or greater to triple superphosphate in terms of agronomic effectiveness.

Some tests were performed in Indonesia with Ciamis phosphates and acid soil (pH 4.5) and Agrotis sp. cultivation and soya, with 100 mgr.P/kg. The EAR was higher in yields with respect to triple superphosphate, increasing the available phosphorus in soil at the same level as TSP. Also the exchangeable calcium was increased and decreased the exchangeable aluminium in greater rate than TSP. In conclusion, phosphate rocks were as effective as TSP. In field trials with different crops and doses of 300 kgs.P_2O_5/He. in degraded soils with this phosphate rock and from other sources,

it was found that their agronomic effectiveness was similar to high reactivity phosphates, recovering soils and proving an economic profitability.
In Mali, with medium reactivity phosphates (Tilemsi), trials have shown that their effectiveness depends on much of rains distribution. Their relative agronomic effectiveness EAR is 80% compared with triple superphosphate, being recommended annual doses of 100-200 kgs / ha. or 300-400 kgs / ha. in crop rotation, applying it on fallow land incorporated with farming at the end of the rainy season. For millet, peanuts, sorghum, cotton and maize crops, in tests carried out by the Rural Economy Institute (IER) and the IFDC 2003, medium and long-term, the Tilemsi phosphate rock is practically equivalent to triple superphosphate per unit of P_2O_5.

In Nigeria, medium-low reactivity phosphates (Sokoto), gave 40% EAR in alfisols with respect to SSP, but it was 102% in ultisols and 162% in oxisols.

Numerous field trials in India (50% agricultural soils with pH less than 5), have shown that phosphate rock from Mussoorie (Uttar Pradesh) can be same or similar to soluble phosphates when pH is below 5.5 in plantations, legumes, rice and corn when there is a good supply of water (Tandon, 1987, Poojari et.al.1988). In rice, the rock was as efficient as the simple superphosphate in acid soil (pH 5.5), while in maize with 5.8 pH, it was obtained 95% of yield whith respect to SSP. In higher pH soils, may be necessary the partial acidulation or mixtures with soluble fertilizer, but in tests conducted at pH 8 with low organic matter and clay-loam texture type ustropept in rice and corn, 52 kg P / ha, the yields were similar to SSP and net profits were marginally better.

In New Zealand, most of the soils are slightly acid (pH 5-6), rainfall of more than 850 annual mm. and crops of ryegrass perennial pastures and white clover, with high roots densities and necessity of continued phosphorus provision, together with calcium affinity and the acidifying effect of nitrogen fixation by legumes. It is therefore suitable for the phosphate rocks application that represent nearly 10% of phosphate fertilizers. Tests performed, recommend the incorporation of phosphate for making eaiser its effectiveness and be comparable with soluble phosphates. Frequently also mixtures of phosphate rock with soluble phosphates are used for increasing water soluble phosphorus and achieving a greater agricultural efficiency.

Tropical soils of South America are mainly ultisols and oxisols, highly acidic, highly formed, of low fertility and high phosphorus retention capacity, so it is important the phosphate rock application. In particular, Venezuela has a factory for producing granular phosphate rock partially acidulated (70% with sulphuric acid) due to 75% of its soils are acid with high precipitation (1000 mm), and has been used for recovering degraded pastures by means of overgrazing and low phosphorus applications. 200 kg. of rock / ha. were applied (together with 100 kg / ha. of urea), increasing crude protein, phosphorous, secondary elements and microelements, weight of animals and milk production, as well as profitability, having an agronomic efficiency similar to TSP.

In Brazil, phosphate rocks are from igneous origin and therefore with low reactivity and low rate of agronomic efficiency, obtaining EAR below 50% with respect to the soluble phosphates TSP in several annual crops. Therefore either greater reactivity phosphates are imported or used termophosphates (calcination with basic slag), which give similar EAR to TSP.

In a study performed by IFDC (USA), has been compared the agronomic effectiveness of phosphorus in TSP, Phospal (calcined aluminium-calcium phosphate) and Gafsa (phosphate rock), in rice crops, flooded and unflooded, and in soya crops. TSP has 46% of total P_2O_5, 38% of water-soluble P_2O_5 and 8% of P_2O_5 soluble in neutral ammonium citrate. Phospal has 34% of total P_2O_5, 9% of P_2O_5 soluble in neutral ammonium citrate, and 2% soluble in citric acid, 2% soluble in formic acid, and 7% iron. Gafsa has 30% of total P_2O_5, 5% of P_2O_5 soluble in neutral ammonium citrate, and 2% soluble in citric acid and 2% soluble in formic acid.

The parameters controlled were the grain and straw production. Neutral and basic soils have been used. At the end of the study we get the following conclusions:

- Phospal is more effective for flooded than for unflooded rice.
- Phospal is more effective than Gafsa in neutral and alkaline rice soils.
- Phospal is less effective than low doses of TSP phosphorus but when doses are high it is similar for rice, and in alkaline soils for unflooded rice is similar at any dose.
- Phospal is more effective than TSP and Gafsa in alkaline soils containing low assimilable iron for unflooded rice and soya.
- Phospal may be effective for the cane development in neutral and alkaline soils.

With respect to the Phospal agronomic effectiveness in alkaline soils, in rice, it is slightly lower to TSP, but much greater than Gafsa.

In unflooded rice and soya, in soils deficient in iron, the performance of Phospal is better than TSP and Gafsa, thanks to its iron supply, but being necessary high doses.

Therefore, despite the low water-solubility of phosphorus contained in Phospal, its agronomic efficiency in alkaline soil is slightly inferior to TSP, and highly superior to the Gafsa phosphate, even though it has half of phosphorus soluble in neutral ammonium citrate than Phospal. In short, in alkaline soils, the effectiveness of Phospal is similar to a high water-solubility phosphate.

Regarding the grain yield in unflooded rice, the effectiveness of Phospal is superior to TSP, but must take into account that alkaline soil used was moderately low in iron, and that it limits more the grain filling and production than the straw, especially in unflooded culture that is more sensitive to the iron deficiency, by which the iron content in Phospal gave better results.

In short, there is observed an agronomic efficiency (production of grain and biomass) similar between Phospal and TSP, and really superior to the Gafsa phosphate. This is very interesting, taking into account that phosphorus water-solubility of the used TSP is 38%, while the Phospal phosphorus water-solubility is practically non-existing and it has only 9% of citrate-soluble phosphorus.

Therefore, in alkaline soils, a calcined phosphate rock has the same performance than a high solubility TSP. In addition if soil is deficient in iron, phosphate rock becomes agronomically better than TSP.

In summary, we can conclude that phosphate rocks can have a performance similar to soluble phosphates in acid soils, and especially if they have high reactivity. If reactivity is low or soils are alkaline, their efficiency can improve through some techniques such as calcination and partial acidulation.

9. METHODS FOR IMPROVING THE AGRONOMIC EFFICACY OF PHOSPHATE ROCKS.

As we have seen in previous section, in some countries, some techniques have been used for increasing the agronomic efficiency when soil conditions (pH above 6) or the available phosphates are low reactivity (mainly from igneous origin), or simply intends to improve their effectiveness without soluble phosphates costes.

Among all the methods used, may mention the composting of phosphates with organic matters as plant rests or manures, that improve phosphorus solubility and availability by crops, and they are interesting for low fertility and low organic matter tropical, arid and alkaline soils, etc. The composting produces a bacterial micro-flora that makes humic substances and organic acids. The increase of phosphorus release by phosphate rocks is produced by the organic acid action and the organic complexes formation with calcium, iron and aluminium. Important amounts of calcium are adsorbed mainly by fulvic acids, while humic acids form with phosphorus, phosphohumates, which make possible the phosphate rock dissolution. To be applied to soil, available phosphorus increases for crops and makes easier a higher movement in depth therefore to explore roots an upper volume, it is produced a higher absorption by crops. Composting materials determine the effectiveness of the final product. The plant rests together with manures seem to give the best results, having an initial C/N relation of 30-35 and humidity close to 50%. The organic materials and rock proportion, may be 4:1, being improved with molasses and other plant sub-products. The rock solubility can increses in some cases more than 15%, going the soluble phosphorus up in citric acid and water. Mishra and Bangar,1986, proved that in soils with pH higher than 7,5 where it is not expected the dissolution of phosphate rock directly applied, the resultant product of composting was as efficient as simple superphosphate.

Another method that can be used is the inoculation of seeds or seedlings with vesicular-arbuscular endomycorrhizes which are present in most of the crops (except chenopodiaceae, cruciferae, polygonaceae and cyperaceae), and increase the capacity of phosphorus absorption, in such a way that some researchers (Murdoch et al.1967) have concluded that the efficiency is higher with low soluble fertilizers like phosphate rocks. This increse of the efficiency may be up to 30% (Pairunan et al.1980) with respect to non mycorrhizal plants. Trials performed with phosphorus solubilizing microorganisms have also given good results, but they have been done in vitro. Apparently the best results have been obtained combining the inoculation of seeds or seedlings with endomycorrhizal fungi with bacteria and phosphorus solubilizing fungi, for successfully increasing the phosphate rocks reactivity, but much research is still needed for developing systems of proven effectiveness in field.

Another system to increase the effectiveness of phosphate rocks is the termophosphates calcination or formation. To insert the rock in furnaces at high temperatures (900 - 1500 ° C) during 3-7 hours, part of CO_2 is removed, but it is necessary a rigorous control of temperature and time of calcination for favouring reactivity.This process makes possible to break the crystalline structure and to increase the material solubility, increasing the assimilable phopshorus percentage for plants. In some occasions it is performed a fusion with basic slag, magnesium silicates, sodium or magnesium carbonates, etc. For acid soils with high phosphorus retention capacity, they make possible to block phosphorus fixation by means of silicon.

Finally, and such as has been mentioned in previous part, when rocks have a limited reactivity or relative high pH (higher than 5,5-6), the phosphates agronomic efficacy may significantly improve by means of a basic chemical process.

The partial acidulation consists of making react phosphate rocks with sulphuric or phosphoric acid in amounts lower than the needed for producing triple or simple superphosphate respectively. They are an economic mean for improving the agronomic efficiency of phosphate rocks, with more reduced costs than superphosphates or ammonium phosphates, with lower consum of acid and energy per unit of phosphorus in the product. Besides, partially acidulated phosphate rocks are usual to have higher concentrarion than TSP. The acidulation level is shown as percentage, in such a way that if it is necessary a fourth part of sulphuric acid, would be called for example PRA-25. When there is used phosphoric acid which contains water-soluble phosphorus, the final product will contain more total phosphorus and more water-soluble phosphorus than the original phosphate rock, on the other hand with sulphuric acid decreases the total phosphorus, but increases the water-soluble one. Normally, acidulations of 30-60 % are those that produce the maximum soluble phosphorus per unit of acid. When acidulation is performed with phosphoric acid it is produced a soluble monocalcium phosphate and a rock fraction that it does not react, called residual phosphate rock. The soluble fraction quickly favours the root development and the phosphorus exploration and absorption by crops, and the rest of the rock is going to be solubilized, giving a gradual supply status. When acidulated with sulphuric acid, there is also calcium sulphate which may difficult the residual phosphorus dissolution, so the drying phase must be controlled.

Normally all the factors that increase the agronomic effectiveness of partially acidulated rocks are the high reactivity, the particles fineness, the chemical properties of soil, especially pH, the phosphorus adsorption by soil, the phosphorus absorption by roots, the growth period of crops, etc. Increasing the adulation increases the soluble phosphorus and the agronomic effectiveness, but the cost of production should be assessed.

We can say that phosphate rocks at 40-50 % acidulation with sulphuric acid and at 20-30 % with phosphoric acid, are as efficient as totally acidulated superphosphate.

For soils with high pH (6,5-8), phosphate rocks partially acidulated may be as efficient as superphosphate, although with phosphoric acid would that be up to 50% acidulation.

The quick use by crops of monocalcium phosphate formed thanks to a partial acidulation, favours a large root development and phosphorus absorption. To dissolving this monocalcium, it is formed H_3PO_4, which reacts with the residual phosphate rock, more easily dissolved.

They can also be prepared blends of phosphate rocks partially acidulated with soluble superphosphates for example 1:1 relation, for increasing the water-soluble phosphorus proportion or when the partial acidulation is not suitable with sulphuric containing iron and aluminium oxides, being able to be compacted this blend, or a simple physical blend. In soils with high pH (7-8), these blends can operate agronomically in a similar way than soluble forms, economizing costs, using simple or triple 1:1 or 2:1 rock/superphosphate proportions. In field trials we have obtained an increse of the rock dissolution superior to 50% with respect to the rock applied alone, with important increases in the phosphorus absorption by crops, mainly by a higher volume explored by roots thanks to the water-soluble phosphorus, which makes easier the rock dissolution.

10. OTHER METALS PRESENT IN PHOSPHATES

Phosphates contain as well as phosphorus, also calcium, some amounts of magnesium, and microelements such as zinc and molybdenum in small quantities, but of agronomic interest.

Regarding the undesirable metals such as cadmium, some studies suggest that its absorption by plants from the phosphate rock is significantly lower than the absorption in water-soluble phosphate fertilizers coming from the same phosphate rock. The cadmium reaction in the soil treated with phosphate rock is quite different from that of the water-soluble phosphate fertilizers due to cadmium is connected to the apatite (Sery and Greaves,1996) in the phosphate rock and it is water-insoluble. Iretskaya *et al.* (1998) informed that high reactivity phosphate rock of North Carolina containing 47 mg Cd/kg was as effective for increasing the non-irrigated rice grain yield as the triple superphosphate coming from the same phosphate rock, but the cadmium concentrations in the rice grain when treated with phosphate rock, was only half of that measure with simple superphosphate.

Some phosphate rocks may contain a significant amount of radioactive elements, for example phosphate rock from Minjingu (Tanzanía) contains 390 mg uranium/kg compared with 12 mg U/kg of the phosphate rock from Gafsa (Túnez). Due to the phosphate rock from Minjingu is highly reactive and agronomically and economically suitable for its direct application into acid soils for the agricultural production (Jama *et al.*, 1997; Weil, 2000), there has been interest in knowing the safety in using this phosphate rock. Therefore, some samples of soil and plants treated with this phosphate rock were collected by the International Council for Research in Agroforestry (ICRAF) and sended to the International Atomic Energy Agency (OIEA) for measuring their radioactivity. Results shown that the soil and plant sample radioactivity were almost the same as benchmark radiation levels.

Most of the phosphate rocks also have high fluor (F) concentrations in apatite minerals, often surpassing 3% weight (250 mg F/kg P). An excessive F absorption is connected to the damages caused to grazing livestock due to fluorosis. McLauhglin *et al.* (1997) reported that there weren't significant differences in F contents in pastures fertilized with simple superphosphate containing 1,7% of F and pastures treated with phosphate rock coming from North Carolina containing 3,5% of F or among places that have received both fertilizers. F concentrations in pasture were normally lower than 10 mg F/kg and often close to the detection limit for the analysis technical (1 mg F/kg). They concluded that it is unprobable that the fluor absorption by plants, in most of soils, causes problems to grazing livestock.

11. SPECIFICATIONS OF OUR ROCK PHOSPHATE DEPOSITS AND CHARACTERISTICS

Phosphate rock extracted from our deposits, has a sedimentary origin, and therefore, it has a medium-high reactivity with a high degree of isomorphic substitution of carbonate in the crystalline structure of the apatite phosphate, and a high amount of carbon dioxide and organic carbon which increase the internal porosity and favours the phosphorus dissolution, just like a high neutralizing value that decreases the exchangeable aluminium in acid soils, increasing the nutrients assimilation with a light increase of pH due to its corrective effect, and the following specification:

Declared content:

Total Phosphorus pentoxide (P_2O_5)	30-31 %
Phosphorus pentoxide (P_2O_5) soluble in 2 % formic acid	7 %
Phosphorus pentoxide (P_2O_5) soluble in 2 % citric acid	6,5 %
Phosphorus pentoxide (P_2O_5) soluble in neutral ammon.citr.and water	6 %
Calcium oxide (CaO)	37 %
Magnesium oxide (MgO)	0,1 %
Calcium carbonate ($CaCO_3$)	30 %
Organic carbon(C)	1 %
Carbon dioxide (CO_2)	12 %
Neutralizing value	33 %
Silicon (SiO_2)	5 %
pH	7
Humidity	7 %

12. RATE AND TIME OF APPLICATION

It should be expected that phosphorus released by rock must be at least equal to the extracted by crops and the retained by soil in not available form. That is, in soils with a level of medium phosphorus reserves, it is enough to restore crop extractions, while if reserves are low, must be considered also the phosphorus which will be retained in sites of soil fixation. In soils with high phosphorus retention capacity, provisions must increase, reducing them if it retains less phosphorus in the soil.

We obtain the best results with phosphate rock if there are medium or medium-high reserve levels in soils. If levels are low, it will be necessary to performing an initial provision of correctors with high dosages of 500-1000 kgs/ha. for continuing in the following years with maintenance doses.

The maintenance doses, as indicated, will depend on phosphorus retention capacity in soils (CEC), pH, texture, reserve levels, crops and extractions, rainfall or risks, etc.

In general, doses are around 200-300 kgs/ha. per year, but it is necessary to know all the factors previously mentioned for a suitable dosage.

Regarding the phosphate rock localization in soil, due to the scarce general movement of phosphorus, it can be applied on the surface but it is advisable to adding it in annual crops in the first 10-15 cm. of soil, for increasing the contact between soil and rock particles, while in perennial and woody crops, it can be applied on the surface for its gradual integration within the soil profile or in its first 30 cm.

Preferably performing applications before rain or prior to irrigation.

With respect to the application time, in highly acid soils (pH < 5,5) with high phosphorus retention capacity, it is recommended the incorporation of phosphate rock immediately before sowing or planting. In soils with pH 5,5-6 with low phosphorus retention capacity, it is advisable to incorporate the rock at least one month or a month and a half before sowing, for making possible a suitable rock dissolution and its availability for crops.

If presented in granular form, its application is easier with any conventional fertilizer spreader.

13. CONCLUSIONS

As mentioned in previous sections, all the factors that take part in the agronomic efficiency of phosphate rocks are:

- Reactivity (solubilities in weak formic and citric acids).
- High phosphorus substitution for carbonate in the crystalline structure of apatite (substitution relation CO_3/PO_4 in the order of 0,2).
- Low content in calcium and free carbonate (< 10 %) as accessory mineral.
- High carbon dioxide (> 15 %) and organic carbon (> 1 %) content, which increase internal porosity and makes easier phosphorus dissolution.
- Neutral pH which produces a light pH neutralization of acid soils in rhizosphere and decreases the exchangeable aluminium.
- Fine particle size (< 0,15 mm) before granulation.
- Soil characteristics (andosols, oxisols, ultisols and vertisols give better results than alfisols).
- Soil acidity (pH < 5,5-6).
- Climate conditions (rainfall superior than 850 mm).
- Cultivated specie (best response of leguminous and perennial plantations).
- Handling practices of crops (phosphorus incorporation).
- High organic matter content.
- High cationic exchange capacity.
- High phosphorus retention capacity in soils.
- Low levels of calcium and phosphate in soil solution.

Depending on the phosphate rock reactivity and type of soil, for highly acid pH (4,5-5,5), the agronomic effectiveness will be similar or superior than superphosphates. For less acid pH (5,5-6) we will continue to find a good agronomic response similar to superphosphates. In this pH status, if reactivity is low, it may be necessary to improve its agronomic effectiveness by means of grinding or partial acidulation, but it is dependent on the rest of factors, considering that even with low reactivity we can find similar responses to superphosphates. For pH close to neutrality or alkalin (6-8), the agronomic efficiency will depend on the reactivity, but generally it will be necessary to improve their action by means of the partial acidulation (40%), mixed with superphosphates (1:1), or controlled calcination.

Advantages of phosphate rocks direct application in acid soils are:

- Agronomic efficiency similar to soluble phosphates in these soils, with good productive results in all type of crops.
- More prolonged provision of phosphorus for crops, thanks to the gradual release in the soil solution.
- Incorporation of great interest exchangeable calcium for many crops and frequently deficient element in acid soils.

- Reduction of the soil exchangeable aluminium, due to the light neutralization in rhizosphere, therefore decreasing its possible toxicity.
- Corrective action of soil pH, favouring the nutrients assimilation.
- They facilitate the recovering of deteriorate soils due to excessive drainage, exhaustion due to overexploitation, scarce fertilization, recent deforestation, etc.
- Smaller economic cost and higher profitability than soluble phosphates in these soils, becoming a renovable source with high global reserves.

The principal characteristics of Senegalese phosphate are the following ones:

- It has a medium-high reactivity with a high grade of isomorphic carbonate substitution in the crystalline structure of the apatite phosphate.

- It has a high amount of carbon dioxide and organic carbon which increase the internal porosity and favour the phosphorus dissolution.

- It has a low free carbonates content as accessory mineral that makes easier its agronomic action.

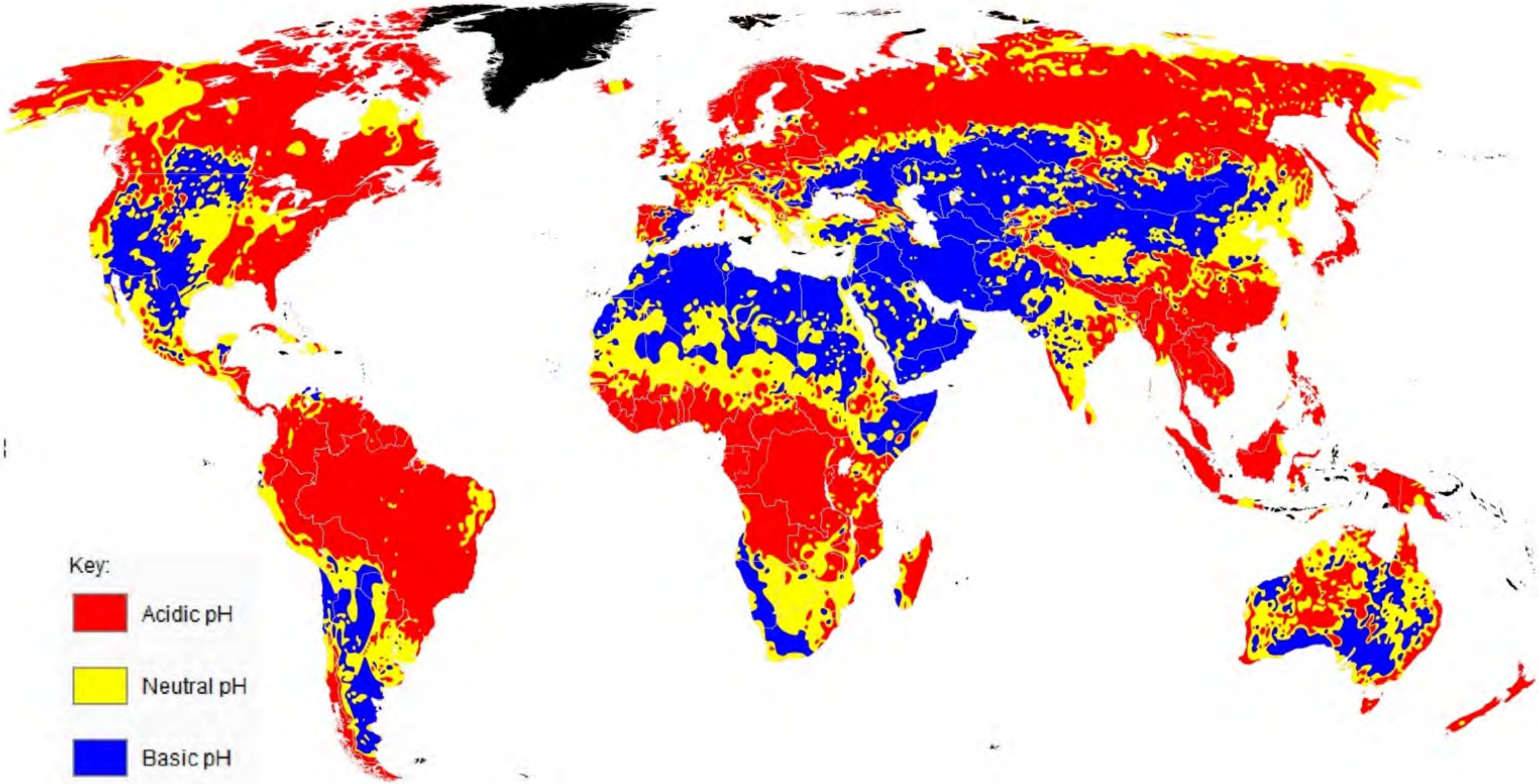
- It has a high great interest exchangeable calcium for many crops and frequently deficient element in acid soils.

- It has a high neutralizing volume which decreases the exchangeable aluminium in acid soils, increasing the nutrients assimilation with a light increase of pH due to its corrective effect.

- It provides a more prolonged supply of phosphorus for crops, thanks to the gradual release in the soil solution.

- It has a fine granulometry that makes easier the phosphorus assimilation in the crops rhizosphere. To more fineness, more contact between phosphate and soil and higher dissolution. In addition, the increase of the particles number per unit/weight of the rock applied, increases the root absorption and therefore the efficiency and favours the rock dissolution, that is, its reactivity.

Attached below a map of the world regions that have acid pH, which can serve as a reference for the direct application of natural phosphates. The areas of greatest interest for the direct application of phosphate rocks are shown in red.


Key:
🟥 Acidic pH
🟨 Neutral pH
🟦 Basic pH

14.REFERENCES

Chien, S.H. 1982. Direct application of phosphate rocks in some tropical soils of South America:a status report. In: E. Pushparajah y S.H.A. Hamid, eds. Phosphorus and potassium in the tropics, pp. 519–529. Kuala Lumpur, Malaysian Society of Soil Science.

Cristancho, J.A.,Hanifi, M.M.,Syed Omar, Rafii, J,M, 2009. Chemical Characteristics of Representative High Aluminium Saturation Soil as Affected by Addition of Soil Amendments in a Closed Incubation System. Malaysian Society of Soil Science.

Diamond, R.B. 1979. Views on marketing of phosphate rock for direct application. In: IFDC, ed. Seminar on phosphate rock for direct application. Special Publication SP-1. Muscle Shoals, Estados Unidos de América, IFDC.

FAO (Organización de las Naciones Unidas para la Agricultura y la Alimentación), 2007. Utilización de las rocas fosfóricas para una agricultura sostenible. Fertilizantes y Nutrición Vegetal.

Frederick, T., Truong, B. y Fayard, F. 1992. Pre-feasibility study: production of modified phosphate fertilizers using Kodjari phosphate rock, Burkina Faso. IFDC-CIRAD-TECHNIFERT.

Ibrahim, S.S.,El-Midany A.A.,Boulos, T.R. 2010. Mechanical Activation of Phosphate rock for fertilizer application. CMRi , Helwan. Egypt.

IFCD .2003.Centro Internacional para la Fertilidad del Suelo y el Desarrollo Agrícola (USA) Direct application of phosphate rock and related technology: latest experiences and practical experiences, S.S.S. Rajan y S.H. Chien, eds. Proc. Int. Meeting, Kuala Lumpur, Muscle Shoals, Estados Unidos de América, International Fertilizar Development Center.

IFCD. 2002. Agronomic Evaluation of Calcined Thies Iron-Aluminium Phophate (Phospal) for crop production.

Iretskaya, S.N., Chien, S.H. y Menon, R.G. 1998. Effect of acidulation of high cadmium containing phosphate rocks on cadmium uptake by upland rice. Plant Soil, 201:183–188.

Jama, B., Swinkels, A. y Buresh, R.J. 1997. Agronomic and economic evaluations of organic and inorganic phosphorus in western Kenya. Agron. J., 89: 597–604.

Lompo, F., Sedogo, M.P. y Hien, V. 1995. Agronomic impact of Burkina phosphate and dolomite limestone. In: H. Gerner y A.U. Mokwunye, eds. Use of phosphate rock for sustainable agriculture in West Africa, pp. 54–66. Miscellaneous Fertilizer Studies. n° 11.Muscle Shoals, Estados Unidos de América, IFDC, Africa.

Maene, L.M. 2001. Direct Application of Phosphate Rock: A Global Perpective of the Past, Presente and Future. IFDC and Malasyan Society of Soil Science (MSSS).

McLaughlin, M.J., Simpson, P., Fleming, F., Stevens, D.P., Cozens, G. y Smart, M.K. 1997. Effect of fertilizer type on cadmium and fluorine concentrations in clover herbage. Aus. J. Exp. Ag., 37: 1019–1026.

Mishra, M.M. y Bangar, K.C. 1986. Rock phosphate composting: transformation of phosphorus forms and mechanisms of solubilization. Bio. Ag. Hort., 3: 331–340.

Murdoch, C.L., Jacobs, J.A. y Gerdemann, J.W. 1967. Utilization of phosphorus sources of different availability by mycorrhizal and non-mycorrhizal maize. Plant Soil, 27: 329–338.

Olsen, S.R., Cole, C.V., Watanabe, F.S. y Dean, L.A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939.

Pairunan, A.K., Robson, A.D. y Abbott, L.K. 1980. The effectiveness of vesicular-arbuscular mycorrhizae in increasing growth and phosphorus uptake of subterranean clover from phosphorus sources of different solubilities. New Phyt., 84: 327–338.

Pearson, R.W. 1975. Soil acidity and liming in the humid tropics. Cornell International Agriculture Bulletin 30. Ithaca, New York, Estados Unidos de América, Cornell University.

Poojari, B.T., Krishnappa, K.M., Sharma, K.M.S., Jayakumar, B.V. y Panchaksharaiah, S. 1988. Efficiency of rock phosphate as a source of phosphorus in rice-groundnut cropping system in coastal Karnataka. In: Seminar proceedings on the use of rock phosphate in west coast soils, pp. 58–63. Bangalore, India, University of Agricultural Sciences.

Sery, A. y Greaves, G.N. 1996. Chemical state of Cd in apatite phosphate ore as determined by EXAFS spectroscopy. Am. Min., 81: 864–873.

Singh, U.2005. Decision support system for direct application of phosphste rock.IFA Regional Conference for Asia and the Pacific.

Tandon, H.L.S. 1987. Phosphorus: research and agricultural production in India. Fertilizer Development and Consultation Organization. New Delhi, Greater Kailash 1.

Truong, B., Pichot, J. y Beunard, P. 1978. Caracterisation et comparaison des phosphates naturels tricalciques d'Afrique de l'Ouest en vue de leur utilisation directe en agriculture.Agron. Trop., 33: 136 145.

Truong, B., Beunard, P., Diekola, K. y Pichot, J. 1982. Caractérisation et comparaison des phosphates naturels de Madagascar en vue de leur utilisation en agriculture. Agron. Trop., 37(1): 9–16.

Weil, R.R. 2000. Soil and plant influence on crop response to two African phosphate rocks. Agron. J., 92: 1167–1175.