

Review

Innovative Phosphate Fertilizer Technologies to Improve Phosphorus Use Efficiency in Agriculture

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Abstract: The main discoveries and advances in the development of industrial processes for the most commercially used phosphate fertilizers in the world (single superphosphate, triple superphosphate, monoammonium phosphate, and diammonium phosphate) occurred from 1830 to 1970, followed by improvements and investments to expand worldwide production capacity. A main opportunity now is aggregating new technologies to conventional phosphate fertilizers so they may become even more efficient in supplying P to plants, which involves research related to the technologies for reduction in soil P losses. Thus, some innovations and technologies have begun to be developed and marketed and continue in continual refinement and adoption in agriculture worldwide to reduce conversion of soluble P applied through conventional phosphate fertilizers into unavailable forms in the soil. This is the case of enhanced efficiency fertilizers, which includes groups of phosphate fertilizers with fixation inhibitors and the chemically modified, controlled-release, blends, multifunctional, and synergistic phosphate fertilizers. The technologies presented in detail in this paper were developed to improve the agronomic efficiency of phosphate fertilization in comparison with conventional fertilizers, with costs varying according to raw materials, production technologies, and distance from the consumer market. This synthesis expands knowledge regarding technologies in use, stimulating the development and application of technologies that increase nutrient efficiency, based on results obtained through suitable methods and equipment along with laboratory, greenhouse, and field results. Increased fertilization efficiency should always be linked with greater economic profitability and the lowest environmental impact, following the principles of sustainability and circular economy. The great challenge for innovation is transforming the knowledge generated regarding fertilizers present in patents and scientific publications into technologies appropriate for the fertilizer market and for adoption in agriculture.

Keywords: phosphorus; enhanced efficiency phosphate fertilizers; phosphate fertilizers with fixation inhibitors; synergistic phosphate fertilizers; chemically modified and controlled-release fertilizers; blends and multifunctional fertilizers



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1. Introduction

The 350-year anniversary of discovery of the chemical element phosphorus (P) was recently commemorated. It was discovered by Henning Brandt, a merchant and alchemist of Hamburg, Germany. The accidental discovery in 1669 occurred in the attempt to produce gold, that is, in the legendary and endless attempt at transformation of cheap materials into valuable ones [1,2]. Brandt's experiments involved distillation of human urine and pieces of silver, which produced a white, waxy, and incandescent substance. He called it "cold fire", which was later called "phosphorus" [3].

In 1776, P was recognized as the 13th element in the historical sequence of discoveries of chemical elements [4]. For one century, the main source of P was urine, until 1770 when the Swedish scientists Ghan and Scheele found P in bones [5].

Years later, in 1835, Gotthold Escher demonstrated the value of ground bones as fertilizer and said that they were “cheap and not very acidic”. After that, the Duke of Richmond suggested that the value of the ground bones as fertilizer was due to the presence of phosphoric acid in their composition [6].

In that same year, Justus Von Liebig, born near Frankfurt, Germany, a scientist who enthusiastically dedicated a good part of his career to chemistry in agriculture, added sulfuric acid to ground bones to make them more soluble to plants. He showed that the P came from calcium phosphates and not from the gelatinous part of the bones. He came to patent a fertilizer that was considered a disaster due to the use of insoluble compounds. When the nutrients were placed in soluble form, the results improved and the fertilizer industry expanded in Germany. In 1840, in his publication *Organic Chemistry in Its Application to Agriculture and Physiology*, Liebig wrote that “finely ground bones that reacted with acids were more effective in plant nutrition”, a theory that stimulated various studies [7].

In England in 1843, 174 years after the discovery of P, the first phosphate fertilizer was commercially produced, developed by John Bennet Lawes, who christened it with the name of “superphosphate”) [8]. Lawes was also responsible for construction of the renowned experimental station of Rothamsted in Harpenden, where he conducted studies in pots and afterwards under field conditions to evaluate the effect of fertilizers on growing plants [9–11]. In 1857, he built the second “superphosphate” factory in Barking Creek, which began fertilizer production in 1860. He also authored a publication with the title *Lawes’ Manures*, which contains information regarding the characteristics, production processes, and use of “superphosphates” on different crops [12].

Interestingly, in this same period, another inventor, the Irish physician Sir James Murray, gave lectures and published a pamphlet with the title *Advice to farmers* in which he described the process to obtain “superphosphates” from ground bones and sulfuric acid [13].

Coincidentally, both published their patents, Lawes (Patent No. 9353) and Murray (Patent No. 9360), related to the production of “superphosphates” on the same date (23 May 1842) [14]. However, Sir Murray had deposited his patents in Scotland weeks before.

Years later, Lawes bought the patent of Sir Murray to avoid any problem of precedence, and the ground bone factories came to be converted to production of “superphosphates” [15]. In 1848, Lawes added to his patent the possibility of substituting ground bones with phosphate rocks. As ground bones became scarce in England, they soon came to be replaced with coprolites [15] and after that with phosphate rocks around 1867.

A fertilizer called triple superphosphate was first produced in small quantities in Germany in the 1870s. This phosphate fertilizer gained importance from 1950 on, because the production of phosphoric acid became economically viable [16]. Before that, for approximately 100 years, most phosphate fertilizer production was of single superphosphate. With the introduction of triple superphosphate, the era of high concentration phosphate fertilizers had arrived. Their consumption peaked in the 1980s; after that, industries came to replace them with ammonium phosphates (MAP and DAP) [16].

As ammonia production became commercially available, the use of ammonium phosphates increased rapidly from 1910 on, and expanded in the 1960s. In 1916, monoammonium phosphate (MAP) was produced by a subsidiary of American Cyanamid Company at Warners, New Jersey, USA, and important advances in the production process were made in Canada in 1933 by Mining and Smelting Co. and by the Tennessee Valley Authority (TVA), Knoxville, TN, USA [15].

Currently, the TVA is called the International Fertilizer Development Center (IFDC) and is located in Muscle Shoals in Alabama, USA. In this important research center, diammonium phosphate (DAP) was also developed, and other technological advances were made for improvements in the production processes of the phosphate fertilizers, e.g., (1) rotary drum ammoniator–granulator, (2) pre-neutralizer, and (3) pipe-cross reactor.

In addition to the fertilizers already referred to, it is important to enrich the context with natural phosphates, fluid phosphate fertilizers, such as polyphosphates, and thermophosphates, produced from thermal processes for solubilization of the P, which originated in Germany and the USA (1940) and later in Japan (1950) [17].

Thus, the main discoveries and advances in the development of industrial processes for phosphate fertilizers most used commercially in the world (single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP), and diammonium phosphate (DAP)) occurred from 1830 to 1970, and they were followed by improvements and investments for expansion of worldwide production capacity.

Currently, one of the big opportunities for scientists and the worldwide fertilizer industry is aggregating new technologies to the conventional phosphate fertilizers so that they become even more efficient in providing P to plants.

Some important characteristics can be listed that should be considered for development of a fertilizer hypothetically considered “ideal”: (1) is inexpensive and efficient; (2) is a biostimulant and adds quality organic matter to the soil; (3) is biodegradable and reduces emissions of gases that cause climate change, from the production process up to after application, according to the principles of Life Cycle Assessment; (4) has adequate chemical, physical, and physical–chemical characteristics; (5) is suitable for different environments and crops, that is, where release of nutrients is synchronized with the absorption curve of the crop, minimizing losses; and (6) has multiple nutrients, that is, has a composition appropriate for the nutritional demand of the crops.

Therefore, the fact is that the challenge is to increase the nutrient use efficiency in agriculture to meet the demand for food of a growing population of living beings on Earth, in conformity with the concepts of circular economy and sustainability widely present in Brazilian agriculture.

Various paths can be taken to increase the agronomic efficiency of phosphate fertilization in Brazilian soils that are generally naturally acidic, of low fertility, and with high capacity for adsorption and precipitation of the phosphate ion. These undesirable reactions reduce the diffusion, the P availability to plants, and the efficiency of the fertilizers [18].

Among the possibilities, we have improvements in the sampling process and in the analytical methodologies of soil analysis, precision agriculture, liming, gypsum application, manners of fertilizer application, irrigation, genetic improvement, adoption of the no-till system or crop–livestock integration, crop succession, and others. In this article, the thematic approach is directed specifically to the technologies for phosphate fertilizers.

It is also important to emphasize that there already is a structure around the world for production of conventional phosphate fertilizers and this will not likely be changed in the short term due to the investments already made. For that reason, we mainly discuss technologies that come to improve the efficiency of fertilizers that already exist in the worldwide production network.

This in no way reduces the importance of development of new production processes and technological routes for phosphate fertilizers and of P recycling, which are global challenges [19].

In this permanent process of developing knowledge, one of the main opportunities for studies related to the technologies for phosphate fertilizers is reduction in P losses in the soil through reactions such as precipitation with iron, manganese, and aluminum in acid soils and calcium in alkaline soils and the adsorption of the phosphate ion [20–22]. For that purpose, some innovations and technologies began to be developed and commercialized and continue in constant refinement and adoption in worldwide agriculture, with the aim of reducing conversion of soluble P applied by conventional fertilizers into unavailable forms in the soil.

Growth in the demand for technologies for phosphate fertilizers that increase the efficiency of fertilization in an economical manner, the establishment of new factories, disruptive innovation, and competitiveness in the sector are factors that should contribute to a greater reduction in the prices of phosphate fertilizers and their technologies. Such

technologies include fixation inhibitors, chemical modification, controlled-release, blends, and synergistic fertilizers. The technologies presented in detail in this paper were developed to improve the agronomic efficiency of phosphate fertilization in comparison with conventional fertilizers, with costs varying according to raw materials, production technologies, and distance from the consumer market. This synthesis expands knowledge regarding technologies in use, stimulating the development and application of these technologies.

2. Worldwide Market of Technologies for Phosphate Fertilizers

This market is not yet very expressive in relation to its potential, but it tends to grow as new factories are established and production costs decline. This makes such fertilizers more accessible to consumers and expands their use on a global scale.

3. Classification of the Technologies for Phosphate Fertilizers

The fertilizers with technologies that lead to improvement in the agronomic efficiency of phosphate fertilization compared with conventional fertilizers are called enhanced efficiency fertilizers.

In general, the phosphate fertilizer that has been chosen by researchers and the industry for improvements in agronomic efficiency is MAP, probably due to greater production in the worldwide phosphate fertilizer network, economic and logistical factors, higher concentration of P, and physical quality in comparison to SSP, TSP, and DAP. However, if they are feasible, nothing impedes the incorporation of new technologies in DAP, TSP, and SSP.

Currently, phosphate fertilizers can be classified in six categories or groups according to the technologies used in their production processes: (a) conventional fertilizers, (b) fixation-inhibitor fertilizers, (c) chemically modified fertilizers, (d) controlled-release fertilizers, (e) blends and multifunctional fertilizers, and (f) synergistic fertilizers (Figure 1).

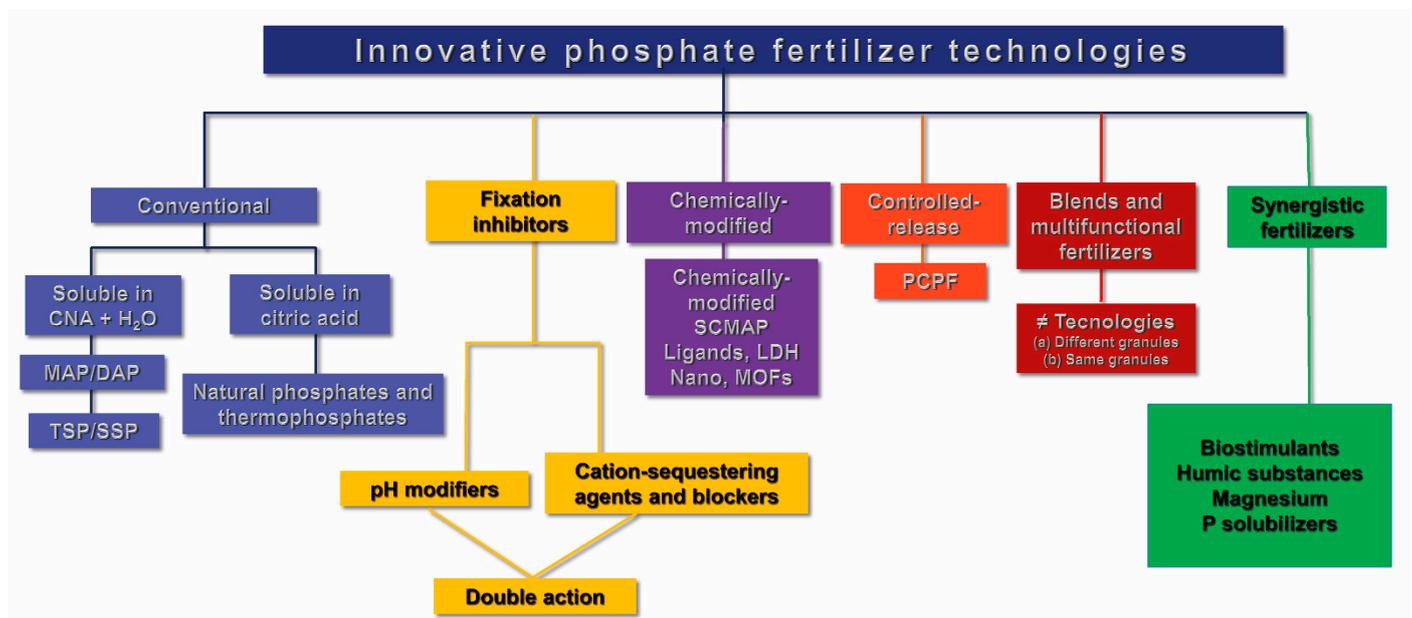


Figure 1. Classification of phosphate fertilizers according to type of technology. Abbreviations: CNA + H₂O: neutral ammonium citrate + water; MAP: monoammonium phosphate; DAP: diammonium phosphate; TSP: triple superphosphate; SSP: single superphosphate; SCMAP: sulfur (S⁰)-coated MAP; LDH: layered double hydroxides; Nano: nanoparticles; MOFs: metal-organic frameworks; PCPF: polymer-coated phosphate fertilizers. Source: image created by the author Douglas Guelfi.

In general, their costs vary according to the costs of raw materials, production technologies, and distance from the consumer market. Fertilizer prices tend to be in the following

increasing order: conventional < fixation inhibitor \leq synergistic fertilizer \leq blends < controlled-release \leq chemically modified \leq multifunctional.

- (A) Conventional phosphate fertilizers: These are fertilizers obtained from phosphate rocks that are solubilized by chemical processes, using sulfuric, phosphoric, and nitric acids or thermal processes. The most used are SSP, TSP, MAP, DAP, thermophosphates, and natural phosphates that are merely ground up, whether followed by partial acidulation or not. We emphasize here that the aim of this publication is not to develop a specific discussion regarding conventional phosphate fertilizers.
- (B) Phosphate fertilizers with fixation inhibitors: These are phosphate fertilizers with additives to reduce reactions of precipitation and adsorption of P in the soil. Figure 2 illustrates the mode of action of this technology. It was created based on the theoretical concepts that are presented in this sub-topic. This group is subdivided into pH-modifying additives and the materials that generate negative charges around the fertilizer granules, which act as agents in sequestering metals such as iron, aluminum, and manganese or blockers of adsorption in the soil. As an example of pH modifiers, we have the materials with acidity neutralizing power, such as oxysulfates, carbonates, oxides, and calcium and magnesium oxides and hydroxides that are applied together with a liquid binder on the surface of the phosphate fertilizer granules. The competing anions (molybdates, sulfates, and silicates), organic acids [23,24], surfactants such as quaternary ammonium [25], and copolymers of the itaconic and maleic acids [26] are compounds that can act as cation-sequestering agents and adsorption blocker.
- (C) Synergistic phosphate fertilizers: These are conventional phosphate fertilizers with the addition of nutrients, microorganisms, nanoparticles, or biostimulants that lead to improvement in the efficiency of P use by plants. As examples, we can cite magnesium, which is a P transporter through cell membranes of the roots, rooting agents associated with soluble calcium in the coating of the MAP to enhance root growth and interception, organic acids, and microorganisms efficient in the solubilization and mineralization of P in the soil.
- (D) Chemically modified phosphate fertilizers: These are P sources that in their production process pass through physical, chemical, or physical–chemical reactions that modify or promote the interaction of P with other chemical compounds that alter its solubility and/or chemical form. That is, the raw materials used in the production process pass through a reorganization in their chemical forms and bonds. Examples of these technologies are the layered double hydroxides (LDH's) [27–29], nanoparticles [30,31], graphene oxide [32,33], and metal-organic frameworks (MOFs) [34,35].
- (E) Controlled-release phosphate fertilizers: These are conventional fertilizers, such as MAP, that have high solubility in CNA + water, to which compounds are added for coating the granule, which serve as a physical barrier and control the flow of P through the coating by diffusion. There are several compounds that can be used for the coating, such as elemental sulfur (S^0), plastic resins, thermoplastics, polyurethane [36,37], polyethylene [38], polyesters, and others [39,40]. The choice of the coating suitable for the phosphate fertilizers is a long and diversified route for innovation in fertilizers. An ideal controlled-release fertilizer should be covered with biodegradable materials that allow suitable control of the release of nutrients under different environments and growing conditions. The nutrient-release curve should be similar to the phosphorus absorption curve of the crop in which the fertilizer is applied to maximize uptake by the plants and reduce P losses. The controlled-release fertilizers have a release rate of the nutrient from inside the coating to the soil basically affected by the type and thickness of the coating, the form of application on annual and perennial crops (incorporated or broadcast on the surface), soil temperature and moisture, and consequently, rainfall amounts. Therefore, the longevity or the time of release of the nutrient from the fertilizer to the soil is an important characteristic of this type of

technology and can vary from days, months, or even to years, depending on the type of product and manufacturer.

- (F) Blends and multifunctional fertilizers: Blends are produced from physical mixture of conventional phosphate fertilizer granules and those that have some type of technology, as for example, controlled-release fertilizers. Physical mixture is made at different proportions among the fertilizers, which are pre-defined and in accordance with the absorption curve of the crop and their technologies. The proportion of conventional fertilizers and controlled-release fertilizers are the main factors that affect the time of release of P from the fertilizer to the soil and determine the final price of the blends. Multifunctional fertilizers have the most diverse types of technologies, though used on the same fertilizer granule through coating and/or granulation.

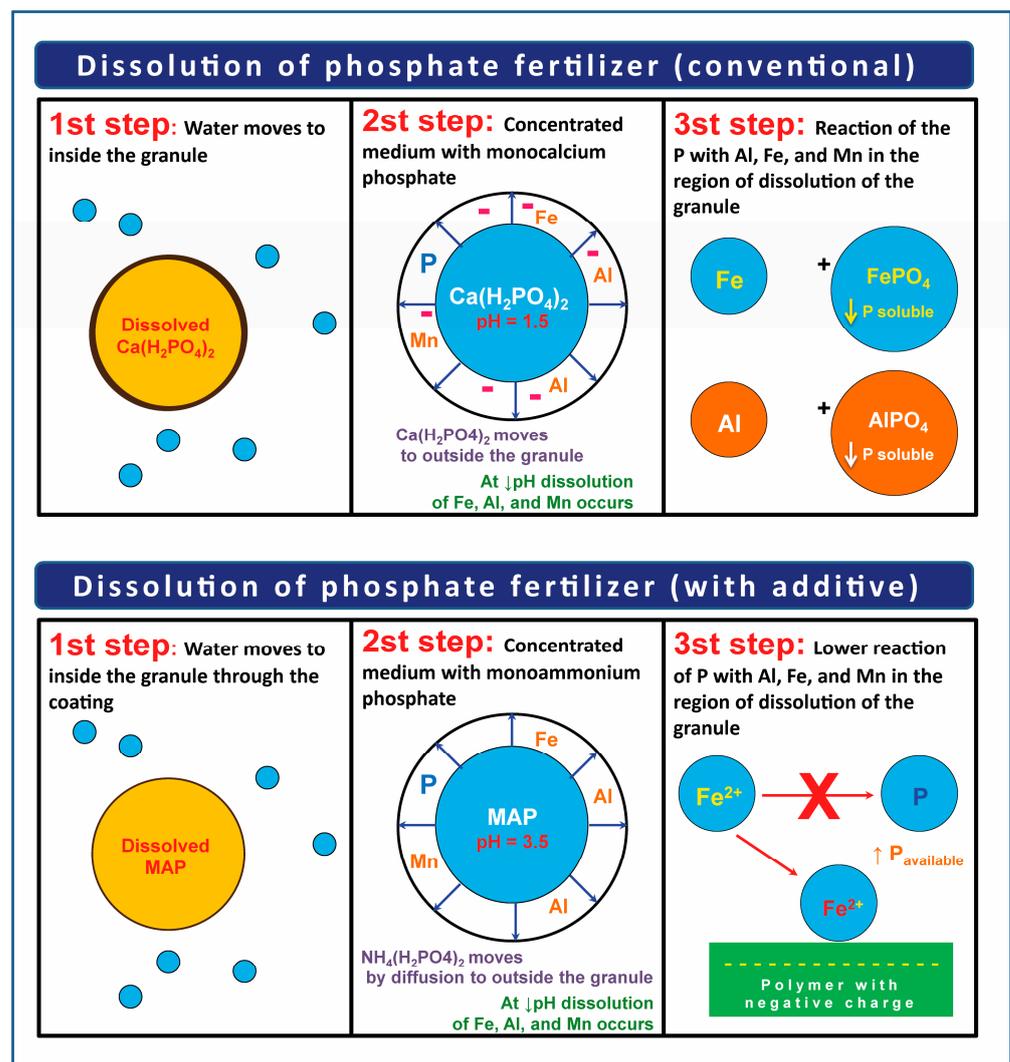


Figure 2. Conceptual representation of the mode of action of the pH modifiers or materials with negative charge used as additives in comparison with conventional phosphate fertilizers. Source: image created by the author Douglas Guelfi.

3.1. Phosphate Fertilizers with Fixation Inhibitors

3.1.1. pH Modifiers

The pH plays a fundamental role in the chemical reactions that control P availability and root growth and interception. The pH modifiers are used in the coating or in the granulation of phosphate fertilizers with the function of increasing (generating OH^-) or lowering (generating H^+) the pH in the microregion of dissolution of the granules. In

addition, they can create a microregion more conducive to root growth due to neutralization of aluminum (Al^{3+}) and to supplying calcium (Ca^{2+}) and magnesium (Mg^{2+}) [41].

The increase in pH can lead to a reduction in precipitation of P with Fe and Al and in adsorption. In this context, this increase would also raise the solubility and the availability of the compounds containing P. However, in soils of areas with surface application of amendments to correct soil acidity and with the surface layer (3 to 5 cm) more alkaline ($\text{pH CaCl}_2 > 5.6$), the results may be more limited (data observed by the main author of the present article).

In general, for production of these types of additives, there is a liquid raw material, a binder, and another solid that are the materials that are to adhere to the granules, such as carbonates, oxides, hydroxides, oxysulfates, and silicates.

The silicates not only increase the pH, but also release silicon, which is a potential anion competitor with the phosphate (H_2PO_4^-) for positive charges in the soil [41]. This can also occur with other materials that have anions, such as molybdate (HMoO_4^-), sulfate (SO_4^{2-}), and fluoride (F^-) depending on their concentration in the fertilizer, solubility, and the intensity of interaction with the positive charges of the soil, acting as adsorption blockers. In this context, it is important to emphasize that the application of low solubility silicates has a limited effect on the competition for positive charges with the phosphate, due to the delayed release of the silicate anion to the soil solution.

The carbonates, oxides, hydroxides, and oxysulfates of calcium and magnesium or substances containing micronutrients such as zinc (Zn) and manganese (Mn) are solubilized a bit more quickly, because the phosphate fertilizers acidify the region where their dissolution occurs. Initially, in the end, reduction in precipitation with Fe and Al occur, as well as in the toxicity of the Al^{3+} the plants and increase in the availability of the accompanying anion present in the alkalinizing materials, with these effects associated with a gain in negative charges.

The amount added to the fertilizers and the reactivity of the pH modifiers are preponderant factors for acidification around the granules. To this we may add that for each 1% of CaCO_3 (100% Total Neutralizing Power—TNP), MgCO_3 (119% TNP), CaO (179% TNP), MgO (248% TNP), Ca(OH)_2 (135% TNP), Mg(OH)_2 (172% TNP); CaSiO_3 (86% TNP), and MgSiO_3 adhering as a coating to the MAP, there is the addition of the equivalent of 1.00, 1.19, 1.79, 2.48, 1.35, 1.72, 0.86, and 1.00 kg of pure CaCO_3 for each 100 kg of MAP [42].

The pH modifiers with low values in their dissociation constant and in their solubility may take a long time to change the pH around the granules of the fertilizers after their application in/on the soil.

In the production process of these additives, the liquids generally have the function of making the solids adhere to the surface of the fertilizer granules; that is, they act as binders and coloring agents, and may also have other functions, such as that of surfactants (Figure 3). The liquid:powder ratio is important for adequate adherence of these materials. Depending on the raw materials used, 10 to 50 kg of additive may be adhered to or coating the granules per ton of fertilizer (data observed by the main author of the present article).

Granulation is another interesting option to add greater quantities of these additives to the phosphate fertilizers, but this option is less used in Brazil. China is currently the largest producer of granulated mixtures.

In some products the strategy is the opposite, that is, acidifying the region of granule dissolution. Acidifying materials such as elemental sulfur (S^0) are granulated with the ammonium phosphates (MAP and DAP) to generate acidity (H^+) and supply sulfur to the plants, according to the reaction: $\text{S}^0 + \text{CO}_2 + \frac{1}{2} \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow [\text{CH}_2\text{O}] + \text{SO}_4^- + 2\text{H}^+$.

Therefore, the acidification potential of the S^0 is -6.25 kg of pure CaCO_3 per kg of S^0 . For example, the application of MAP coated with 10% S^0 at the rate of 250 kg ha^{-1} would generate acidity for which 25 kg of limestone (TNP = 100%) would be necessary to neutralize it.

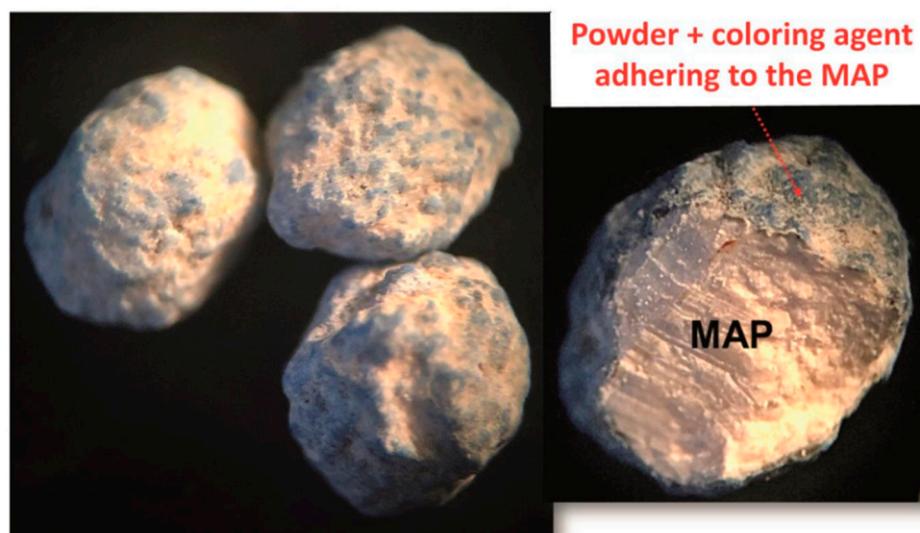


Figure 3. Optical microscope images of the MAP + powder (sulfate or carbonate) + adhesive agent + coloring agent. Source: image created by the author Douglas Guelfi.

Relevant information is that the dissolution of MAP in the soil is rapid and the oxidation of S^0 is slower and depends on various factors [43,44].

The mixture of S^0 with natural phosphates or with thermophosphate is an option for increasing its solubility, due to the acidity generated by the S^0 . In this case, sulfate and ammonium nitrate are also alternative options to S^0 because they generate acidity for dissolution of the P. The mixture of phosphate with ammonium and/or sulfate can improve the solubility and mobility of the P. This occurs due to the acidity generated (H^+) in the first step of nitrification of the ammonium to nitrite in the soil: $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+$. For each 100 kg of sulfate and ammonium nitrate applied, acidity is generated for which 110 and 60 kg of pure $CaCO_3$ is necessary for their neutralization, respectively, which is an opportunity for the development of granulated mixtures.

Another possibility is coating phosphate fertilizers with S^0 , which leads to modification in the MAP release rate and reduction in pH (Figure 4). The P release rate and the acidification brought about by coating the phosphate fertilizer with S^0 occurs in accordance with the thickness, type, and quality of the coating; with the activity of the microorganisms responsible for the oxidation of the S^0 , that is, for the oxidation rate of the S^0 ; and with soil pH, temperature, and moisture.

The technologies with S^0 in phosphate fertilizers have been studied since 1940 [45–48]. One of the important factors is that the oxidation rate of the S^0 is slower than the dissolution of the phosphate fertilizer, which ends up making the S^0 layer serve more as a physical barrier than as an immediate source of acidity.

Granulation is another technology that opens a series of possibilities for innovation in phosphate fertilizers co-granulated with different pH modifiers (Figure 5); for example, we have MAP enriched with S^0 in the ammonia and phosphoric acid reactor and granulated MAP with micronized S^0 and micronutrients).

Products of this type are imported and commercialized in Brazil and they are composed of conventional MAP produced with micronutrients and sulfur in two forms: sulfate (SO_4^{2-}) and elemental sulfur (S^0). Basically, the strategy is to introduce the micronutrients, mainly in the form of oxides and the raw materials containing two chemical forms of S in steps of the production process (which occurs in the pipe-cross reactor) of the conventional MAP. Therefore, the final product is an MAP with two forms of S and micronutrients [49,50].

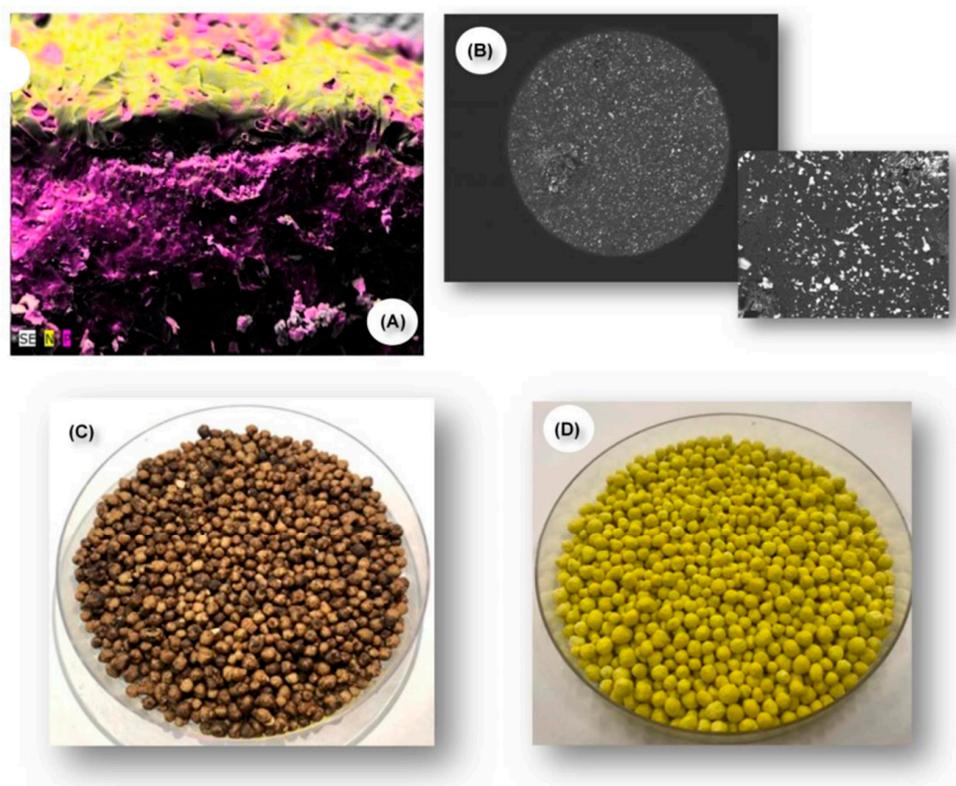


Figure 4. Electromicrography by scanning electron microscopy (SEM) of a granule of MAP coated with elemental sulfur (S^0). Purple coloring = phosphorus; yellow coloring = layer of coating with S^0 (A) and of the granulated MAP with micronized S^0 (B); optical microscope images of the MAP enriched with elemental sulfur (S^0) in the ammonia and phosphoric acid reactor (C); optical microscope images of the MAP + coated with S^0 (D). Source: image created by the author Douglas Guelfi.

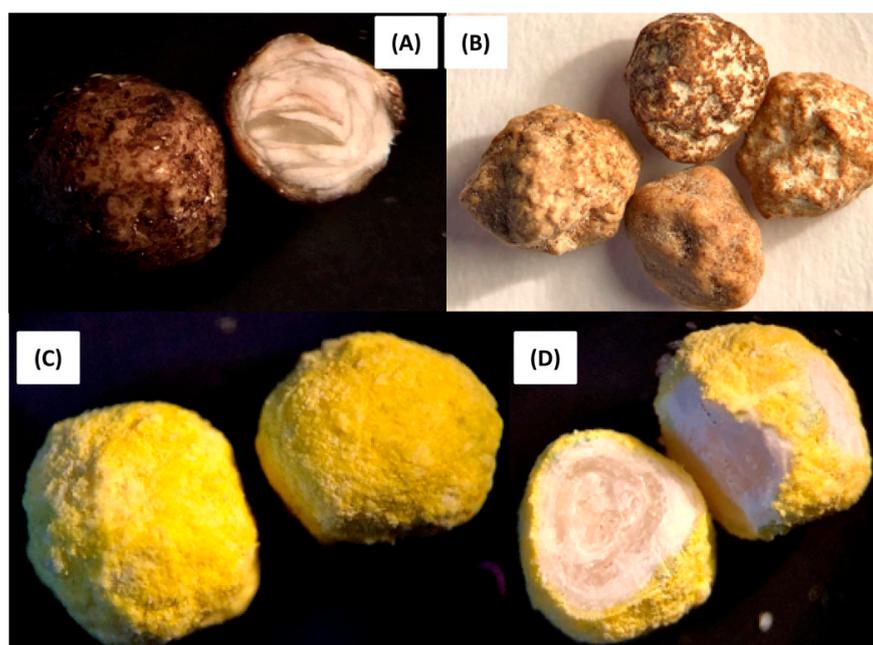


Figure 5. Optical microscope images of a granule of MAP enriched with elemental sulfur (S^0) in the ammonia and phosphoric acid reactor (sliced granule—A); granulated MAP with $S^0 + SO_4^{2-}$ and micronutrients (intact granule—B); MAP coated with S^0 (intact granule—C; and sliced granule—D). Source: image created by the author Douglas Guelfi.

An interesting possibility would be to solubilize the magnesium oxide together with the MAP or add it in the acidulation of fertilizers such as SSP, TSP, and the ammonium phosphates, since magnesium availability has been a limiting factor in some soils cultivated in Brazil.

Among numerous other possibilities, it would be possible to produce a phosphate fertilizer in the form of a granulated mixture with each granule composed of MAP (fast dissolution), fused magnesium phosphate (alkaline, with slower dissolution, and with silicon, calcium, and magnesium), S^0 (source of S and slow dissolution and generator of acidity), and natural phosphate (source of calcium and slow-dissolution phosphorus). This fertilizer would have different sources and times for P dissolution. In this case, the extent to which the raw materials of lower solubility are ground plays a fundamental role, to which may be added the possibilities of technologies for production of nanoparticles and the importance of their interfaces with the solubility of the nutrients.

The conventional MAP production process, the quantity added, and the solubility of the pH modifiers and the soil characteristics (as for example the CEC) in the surface layers control the intensity and the duration of the increase in pH near the fertilizer granules.

The pH of the conventional phosphate fertilizer is an important characteristic in idealization of its technologies. There are diverse raw materials, processes, and production technologies available that have been studied to change soil pH in the microregion of the dissolution of the phosphate fertilizer granules as a strategy to improve fertilizer efficiency. The conventional MAP production process itself can also lead to a final product with different pH values according to each manufacturer.

3.1.2. Cation-Sequestering Agents or Blockers

The pH, cation activity, soluble anions, and the balance of charges in the soil affect the availability of P to plants. Hypothetically, the cation-sequestering additives act by generating negative charges around the phosphate fertilizer granules to retain cations that precipitate with the P (Figure 2). In acid soils, these cations are Fe^{2+} , Al^{3+} , and Mn^{2+} , and in alkaline soils, Ca^{2+} and Mg^{2+} . In addition, the charges generated can help repel the phosphate ion.

Thus, we should reflect on the capacity of materials that generate negative charges in sequestering or retaining cations, and the question that arises is as follows: what would be the quantity of exchangeable aluminum (Al^{3+}) that can be retained in a cation-sequestering agent with $1100\text{ cmol}_c\text{ kg}^{-1}$ of negative charges on the surface added to the conventional MAP at 2%? As an example, we determine a rate of $250\text{ kg of MAP ha}^{-1}$ with this additive for cation sequestration (2%).

Furthermore, suppose that the density and the effective CEC of the soil are equal to 1.1 g cm^{-3} of $4\text{ cmol}_c\text{ dm}^{-3}$. The phosphate fertilizer is applied in the planting furrow, entering in contact with 2% of the soil volume of the 0–20 cm layer, which is a total of $44,000\text{ dm}^3$ of soil, with CEC in the region of contact of the fertilizer granules equal to $176,000\text{ cmol}_c\text{ dm}^{-3}$.

In this soil, according to its chemical analysis, there is 1 cmol_c of $Al^{3+}\text{ dm}^{-3}$. We would have $44,000\text{ cmol}_c\text{ dm}^{-3}$ of Al^{3+} to react in this microregion. The application of 250 kg ha^{-1} of MAP with 2% of the additive would increase negative charges per kg^{-1} by 5000 cmol_c . Even so, $39,000\text{ cmol}_c$ of $Al^{3+}\text{ dm}^{-3}$ would be left over for reaction with the phosphate ion, without counting other competing cations present. In other words, the additive would capture approximately 11% of the Al^{3+} existing in the soil. The charges generated by the additive would increase the CEC around the fertilizer granules by 2.8%; what initially was $176,000\text{ cmol}_c\text{ dm}^{-3}$ would increase to $181,000\text{ cmol}_c\text{ dm}^{-3}$. In this respect, materials with high density of charges should be developed so that the effects are more pronounced.

Some of the chemical compounds present in this category of technologies propose a second mode of action, here called blockers. They are compounds present in the additives that would act, as the name itself states, by blocking part of the adsorption sites of P in the

soil. Theoretically, these additives would promote reduction in P adsorption and increase in diffusion of P in the direction of the roots for plant nutrition.

The main chemical compounds classified as cation-sequestering agents or blockers have the following in their composition: (a) organic acids, such as fulvic and humic acids [23,24]; (b) anionic surfactants and/or cationic and chelating surfactants [51,52]; and (c) copolymers of the itaconic and maleic acids [26]. Thus, all compounds with the presence of a high number of negative charges on their surfaces would be probable substances capable of retaining cations around the fertilizer granules. Furthermore, the positively charged compounds would promote blocking of the P adsorption sites.

In general, additives are applied to soluble phosphate fertilizers such as MAP and DAP. They can be formulated as liquids or be composed of liquids that are an adhering and coloring agent for another additive in powder form, that is, a mixture of liquid and powder. These formulations are applied in fertilizer mixers adapted for that purpose.

A hypothetical example would be the addition of an anionic surfactant and liquid organic acids associated with the nutrient source in the powder granulometry. The solid phase can also be some raw material in the micronized form or even nanoparticles containing compounds such as magnesium, zinc, or manganese oxides, sources of boron, calcium, and sulfur, among other processes possible for development of the most varied technologies.

There are diverse scientific articles in worldwide scientific literature that discuss the effectiveness of this type of technology [26,46,48,53–56].

One of the substances called cation-sequestering agents or blockers that are added to the phosphate fertilizers are fulvic and humic acids [24,48,57,58]. They originate from soil organic matter, water, and geological deposits and are defined as a complex mixture of poly-disperse materials formed by chemical and biochemical reactions during the decomposition and transformation of plants and organisms [59].

The hypothesis is that the humic substances can act in improving P availability through adding it to phosphate fertilizers by different forms: (1) as materials capable of exchanging cations; (2) as blockers of phosphate adsorption sites; (3) through reduction in P precipitation; (4) through formation of compounds containing phosphate and humic acids; (5) by improving growth of the root system; and (6) as stimulants to soil microorganisms that promote P solubilization and mineralization in the soil and are hormonal stimulants to plants [57,58].

In this sphere, studies are important for quantifying the efficiency of organic acids for improving the efficiency of phosphate fertilization. Nunes et al. [60] quantified P diffusion in Petri dishes over time and the agronomic results of the MAP coated with humic substances, magnesium, and micronutrients. Their results showed an increase in P diffusion only for the MAP coated with humic substances and in the time of 1 h after contact of the fertilizer with the soil. At the end of the 18 days, there was no increase in P diffusion or in maize yield in two experiments performed under field conditions [60].

However, in another diffusion test with these same technologies [60] and carried out according to the methodology proposed by Benbi and Gilkes [61], the results show an increase in P diffusion and movement in horizontal and vertical directions according to soil texture.

The humic substances, magnesium, and micronutrients did not have any effect on P release from the MAP. The organic materials added to the MAP did not lead to reduction in their salinity. The values of the salt index were different for the conventional forms of MAP1 (brown) and MAP2 (white), probably due to their different production processes. The addition of magnesium oxide with the humic substances in the coating of the MAP brought about higher values of pH (5.3) and hardness of the granules compared with the conventional MAPs [60].

Questions related to humic substances arise due to the amount applied to the fertilizers (1% to 5%) and economic viability. Perhaps it is much more practical and efficient to increase the quantity of these compounds in the soil with management practices to increase and

improve the quality of soil organic matter over time than through application in small amounts in fertilizers.

Therefore, the big challenge in relation to humic substances is adequately aligning the scientific results produced under controlled conditions and in the field, as well as to use the knowledge from published articles to transform the commercial products on the market so as to be more efficient and viable [24].

There are already commercial products in Brazil that use phosphate, such as metal, humic acids as complex fertilizers. Superphosphates are granulated together with humic acids. More details are contained in the following publications: Urrutia et al. [57], Degryse et al. [53], Erro et al. [62], and Urrutia-Sagardia et al. [63].

The chelating agents and the anionic and cationic surfactants act in modifying the balance of charges in the region of dissolution of the fertilizer granules, fostering conditions for retaining cations and blocking P adsorption sites. Some examples of ionic surfactant groups are sulfonate (RSO_3^-), carboxybetaine ($-\text{NR}_2\text{CH}_2\text{COO}^-$), sulfobetaine ($-\text{N}(\text{CH}_3)_2\text{C}_3\text{H}_6\text{SO}_3^-$), and quaternary ammonium ($-\text{R}_4\text{N}^+$). In an aqueous solution, the quaternary ammonium can, for example, retain counterions with Fe^{2+} , Al^{3+} , and Mn^{2+} . The chelates would complex these same cations [53].

The scientific results of the copolymers of the itaconic and maleic acids are detailed and extensively discussed in publications [26,46,48,53–56]. These additives that are called antagonistic cation-sequestering agents and P-fixation inhibitors by the manufacturer, together with the controlled-release phosphate fertilizers, are perhaps one of the phosphate fertilizer technologies most studied throughout the world.

The additive with copolymers is applied at the rate of 2.1 L per ton of phosphate fertilizer. The additive is generally applied within a fertilizer mixer equipped with spray nozzles for sprinkling the additive in liquid form onto the granules. The composition of the additive includes sodium salts of copolymers of itaconic and maleic acid (30%) and water (70%). Its main characteristics are high cation exchange capacity ($1000 \text{ cmol}_c \text{ dm}^{-3}$), solubility in water, and biodegradability. The mode of action is through the polymer capturing antagonistic cations in the soil solution around the phosphate fertilizers [26,46,48,53–56].

Therefore, the main difference between the technologies of cation-sequestering agents and the chemically modified fertilizers, which is presented in the following topic, are the time and the location of reaction of the P. In the case of the cation-sequestering agents and blockers, the reactions of retaining and exchange in the soil occur after the dissolution of the fertilizers. In the chemically modified fertilizers, the chemical reactions mainly occur during the production process.

3.2. Chemically Modified Phosphate Fertilizers

The chemically modified phosphate fertilizers pass through physical, chemical, or physical–chemical processes in their production that lead to modifications in the form of P present in the fertilizers and in its interaction with other materials. These modifications may improve the solubility, mobility, time of release or longevity, and absorption by plants. In general, these products are more in the development stage than in commercial use.

The raw materials used in the production process pass through a reorganization in their forms and between chemical bonds and interactions between the phosphorus and different compounds. Examples of these technologies are nanoparticles, layered double hydroxides (LDH's), graphene oxide, and metal-organic frameworks (MOFs).

The interface between the nanoparticles in fertilizers and plant nutrition has been studied for years to clarify how the response of the nanoparticles can improve nutrient use efficiency. The nanomaterials have high specific surface area per unit of volume, indicating the possibility of reaction between the P and the surface of nanomaterials for later release to the soil. From the perspective of solubility, reducing the size of the particles to the nano scale may lead to faster release and mobility of ions in the composition of the nano-fertilizers.

In this context, the use of nano-hydroxyapatites may be an important technological alternative [64–66]. Relevant information on how the nanoparticles can improve the mobility and uptake of P should be available in the near future [48,67,68].

The layered double hydroxides (LDH's), sometimes also called anionic clays, are produced by interspersing layers of hydroxides and the anions, which can be natural or synthetic. These compounds can incorporate anions in their structure in the region between the layers, neutralizing the negative charge of the layers. These anions incorporated in the LDH's are gradually released to the soil solution. The big challenge of this type of product is synchronizing the release of the anions with uptake by plants.

Since its discovery in 2004 up to now, graphene oxide has been studied in numerous sectors, such as the military, aviation, pharmaceuticals, and others. The two-dimensional (2D) arrangement of the carbon atoms creates high surface charge density ($2600 \text{ m}^2 \text{ g}^{-1}$); therefore, graphene oxide can serve as a structure for retaining and releasing the P gradually over time. The big challenge for the use of graphene oxide in fertilizers is increasing its P retention capacity and diminishing its cost, which is currently very high and restrictive for use in the fertilizer industry [48].

The metal-organic frameworks (MOFs) are porous materials that are worked to release nutrients in the soil after their chemical deconstruction, degradation by microorganisms, and hydrolysis by water. They have become a more frequent option in scientific research studies that aim at new phosphate fertilizers for agriculture [34].

3.3. Synergistic Phosphate Fertilizers

The basic principle of synergistic phosphate fertilizers is taking advantage of beneficial associations among fertilizers, biostimulants, microorganisms, and nutrients. Conventional fertilizers receive additives that can be plant nutrients or beneficial chemical elements, biostimulants, and biological materials that create conditions for improving P uptake, the rhizosphere environment, water use efficiency, growth and development, physiological processes, nutrition, nutritional quality, and stress reduction in plants.

Among these additives here called synergistics, we can provide examples to illustrate the concept of this technology by citing the classic effect of the synergism between P and Mg nutrients in the development of technologies for phosphate fertilizers [69]. Mg is a P transporter, and its presence in the microregion of dissolution of the fertilizers improves P use efficiency [70]. In addition, MgO is also a pH modifier.

Algae extracts and humic substances can also act to improve soil structure, increase solubilization of micronutrients, or even change morphology and stimulate root development and microorganism development [71].

Biostimulants are used for production of what are known as biofertilizers. They are substances, excluding nutrients or phytosanitary products, that when applied to plants are able to modify physiological processes so as to provide benefits for their growth, development, and nutrition, as well as for stress reduction. This definition includes substances such as algae extracts, humic substances, amino acids, and plant-growth-promoting mycorrhizae and bacteria [71].

One of the benefits of using biostimulants added to phosphate fertilizers would be improvement in growth of the root system. A root system that is better developed and distributed in the soil profile enhances root interception of P and improves tolerance to water stress.

Another way toward development of technologies for fertilizers is the use of biological agents, such as microorganisms efficient in P solubilization. Microorganisms have different strategies to solubilize P, such as exudation of citric and gluconic acid, change in the pH of the rhizosphere, and mineralization of organic P. It is important to emphasize that the results obtained in the laboratory do not always function as well as under field conditions [72]. The big challenge may be selecting microorganisms that are efficient and resilient and determining percentage values of P of the fraction unavailable in the soil that is solubilized due to the action of the microbiota.

However, the incorporation of biological agents to fertilizers is a route to development of new technologies for improving the efficiency of P use in agriculture [73].

3.4. Controlled-Release Phosphate Fertilizers

These are conventional fertilizers, such as MAP and DAP, but after granulation, the granules are coated to control water penetration, the rate of fertilizer dissolution, and the duration of the period of nutrient release (Figure 6).

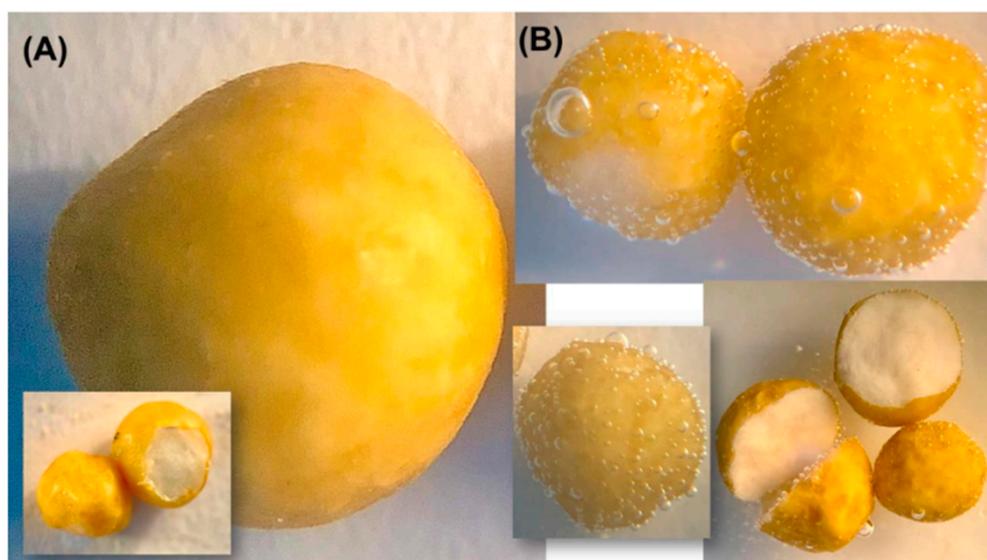


Figure 6. Optical microscope images of the MAP coated by polymers and the granules cut in half (A). Whole MAP granules and granules cut in half in pure water (B). Source: image created by the author Douglas Guelfi.

Diverse natural or synthetic compounds have been evaluated for coating fertilizers, such as natural polymers such as starch, alginic acids, wheat gluten, and rubber and latex in their natural or modified forms. Various synthetic compounds have also been prepared for coating fertilizers, such as polyolefins, polyurethane, polyacrylic acid, polyacrylamide, polysulfonate, polyvinyl chloride, polystyrene, polyacetate, and polydopamine.

The shape of the fertilizer granules, the type of coating, the thickness, uniformity, and quality of the coating, the soil temperature and moisture, and the manner of application (in the plant furrow or broadcast) in the crops control the release and the concentration of nutrients in the solution over time.

The ability of the granules to absorb water and the flexibility of the layer of coating are also important characteristics of the controlled-release fertilizers. The greater the penetration of water and the increase in volume of the granules, the greater the release of the nutrient to the soil is [74,75].

Soil moisture is directly related to the manner of application of controlled-release phosphate fertilizers. Theoretically, in the planting furrow, greater contact with the soil and its moisture would occur, whereas broadcast application would reduce direct contact with the water and, consequently, the period of P release.

The controlled-release fertilizers also affect the range of variation in the salt index and osmotic potential, pH, and electrical conductivity in the soils after their application. Reduction in the salt index and in electrical conductivity is very important because it is related to less damage to seed tissues, seedlings, and roots and the variations in pH can affect the availability and reactions of the nutrients in the region of dissolution of the granules. Furthermore, gradual release of the soluble phosphate fertilizers through the coating can reduce acidification around the granules.

Depending on the material used in the coating, improvements occur in the physical and physical–chemical characteristics in comparison to conventional phosphate fertilizers, such as reduction in caking, powder formation, hygroscopicity, suitability of the angle of repose and fluidity, increase in the hardness, and uniformity of the granules. Therefore, the granule size and the amount and type of coating affect the resistance of the fertilizer granules [60].

For particle size from 3.5 to 4.0 mm, the hardness or resistance to compression of the phosphate fertilizers and their technologies was (A) MAP controlled-release “1” (NP 09-47-00) = 13.02 kgf, (B) MAP controlled-release “2” (NP 10-48-00) = 10.42 kgf, (C) MAP + additive = 8.09 kgf, (D) MAP + humic substances = 8.17 kgf, (E) MAP (white) = 11.24 kgf, and (F) MAP (brown) = 8.09 kgf.

Biodegradability is another important factor in the development of coating for fertilizers [76,77]. Although synthetic polymers have greater resistance and control of nutrient release, their accumulation in the soil can lead to a new form of pollution [78,79].

Release of nutrients occurs by diffusion through the coating. Water (mainly in the form of water vapor) enters the granule through the coating (Figure 7). The vapor is condensed within the granule and dissolves part of it, leading to an increase in pressure within the coating. At this stage, two processes are possible: (a) if the internal pressure is greater than the resistance of the coating, the coating ruptures and releases the nutrient immediately to the soil solution, or (b) if the membrane resists the internal pressure, the nutrient is released by diffusion according to the concentration, temperature, and moisture gradients.

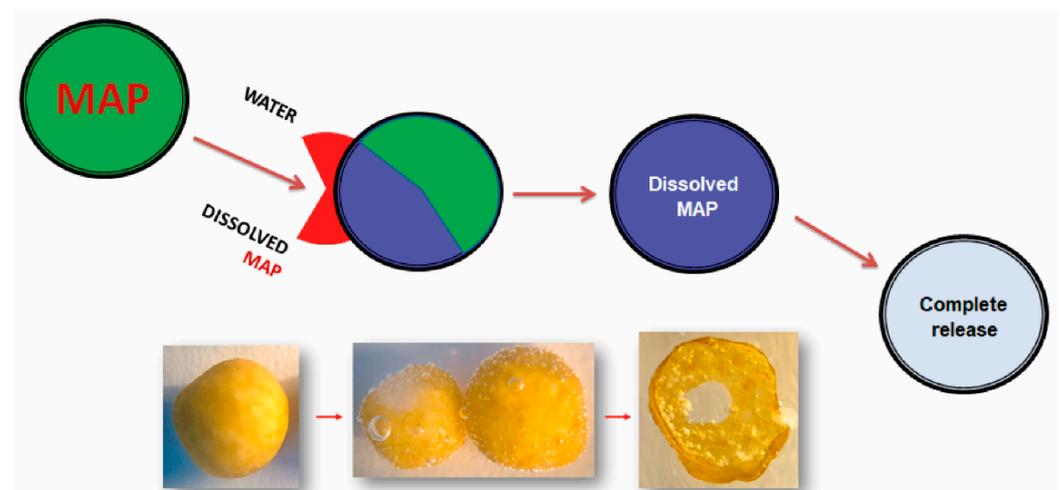


Figure 7. Illustrated schematic diagram of phosphorus release from the controlled-release MAP. Source: image created by the author Douglas Guelfi.

Conceptually, the phosphorus release curve of the fertilizer should be as similar as possible to the phosphorus uptake curve of the crop to be fertilized. The release curves of the phosphate fertilizers and their technologies are shown in Figure 8. The controlled-release MAP with the greatest longevity (NP 09-47-00) and the controlled-release MAP (NP 10-48-00) with the most limited longevity released 40% and 71% of the phosphorus in 28 days, respectively. The conventional MAPs (white and brown), MAP + additive, and the granulated MAP with humic substances released more than 90% of the phosphorus in the first four days, showing lack of control in release of this nutrient.

Determination of the nutrient-release curve of the fertilizers coated with polymers is very important, because there is variation in the phosphorus release rate according to the shape and size of the fertilizer granules; the composition, thickness, structure, porosity, and quality of the coating; the soil temperature and moisture; and the amount of rain in millimeters after application in the soil. Factors such as pH and the ionic force of the soil solution do not affect the time for release of the nutrient from the fertilizers.

Nevertheless, the type of coating used, plastic resin or polyurethane, changed the nutrient-release curve [75].

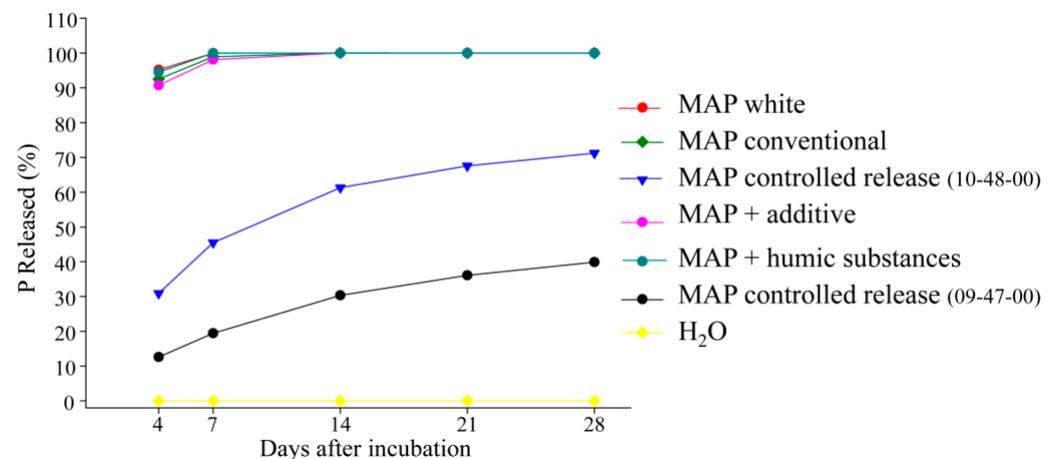


Figure 8. Release of phosphorus in water (25 °C) of phosphate fertilizers and their technologies. Source: Image created from data obtained by the author Douglas Guelfi.

Different methodologies have been used to evaluate fertilizer nutrient release under laboratory conditions and soil conditions [78]. The ISO standards 18644:2016 [80] and 21263:2017 [81] are international references for quantification of fertilizer nutrient release. Measurement of electrical conductivity is another option of an accurate and inexpensive methodology for estimation of P release from conventional phosphate fertilizers and from controlled-release fertilizers and their blends [81].

3.5. Blends and Multifunctional Fertilizers

An alternative for reduction in the costs of increased efficiency fertilizers and for fitting the P release curve to each type of crop is the use of technologies in an integrated manner in the form of blends. Blends are produced from the physical mixture of conventional fertilizers and those with some type of technology in different proportions according to the P uptake curve of the crop and the final cost of the blend, as shown in Figure 9.

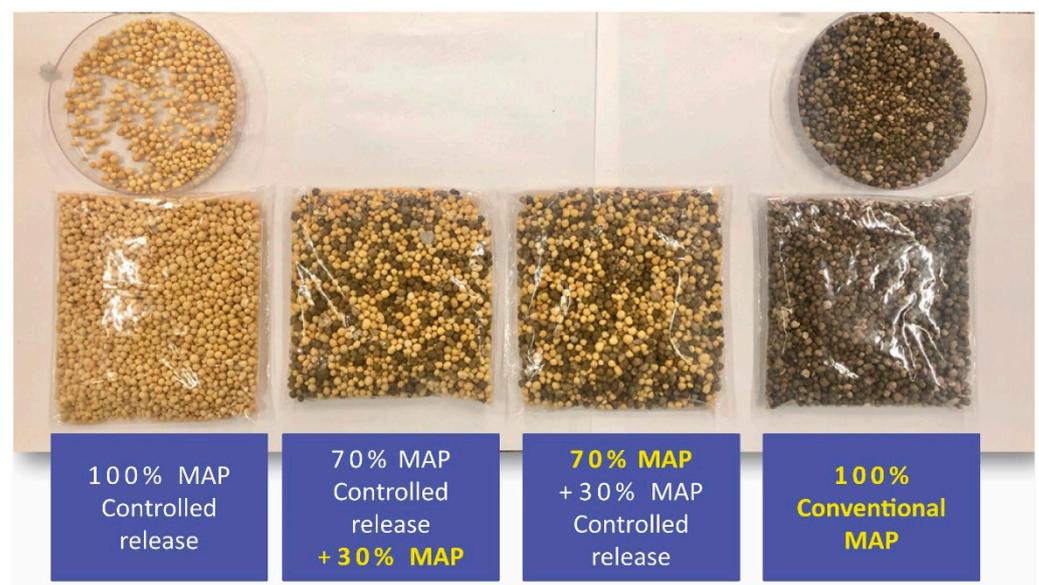


Figure 9. Blends or physical mixture of conventional MAP granules and controlled-release granules. Source: image created by the author Douglas Guelfi.

The physical mixture of controlled-release MAP granules and conventional MAP is a type of blend. Part of the conventional MAP is soluble and meets the immediate demand of P by the crop. The other part, the controlled-release MAP, releases the P gradually, depending on the characteristics of the coating, which affect the longevity or release time of the P.

The fertilizers here called multifunctional are those conventional phosphate fertilizers to which different technologies were aggregated to the same granule in their production process, differentiating them from blends. The compounds can be added through the coating or through processes of granulation in layers, similar to the image of an onion cut in the middle.

Multifunctional technologies can be produced with various layers of raw materials and additives, each one of them with a different function. These functions can be aggregating other nutrients; increasing carbon and organic acids; improving the chemical, physical, and physical–chemical characteristics; binders; surfactants; pH modifiers; granulated raw materials with different solubility of P; nanoparticles; biostimulants; and additives for improving the agronomic efficiency of the P sources for worldwide agriculture.

In this scenario, we have an important path to disruptive innovation that can lead us to achieving the eternal challenge of feeding the living beings that inhabit the Earth.

4. Final Considerations and Future Perspectives

Phosphate fertilizers with fixation inhibitors, chemically modified and controlled-release fertilizers, synergistics, blends, and multifunctional fertilizers are options to be taken into consideration for improving the efficiency of phosphate fertilization in agriculture within a broad context of strategies for that same purpose. The efficiency of these fertilizers can be improved if they are combined with strategies as basic as soil sampling and limestone and gypsum application to more refined strategies, such as the no-tillage system, precision agriculture, and integrated crop–livestock systems. Understanding the relation of the interface of polymers with organic matter and biotechnologies and, above all, dissemination of information regarding the benefits provided by these technologies is also important.

The processes of evaluation of their agronomic efficiency should be very thorough, including studies with methods and equipment suitable under conditions in the laboratory, greenhouses, and the field so that the results may be analyzed in an integrated manner and not in an isolated way, for a careful and reasoned choice of the technologies.

The phosphate fertilizers with fixation inhibitors, chemically modified and controlled-release fertilizers, synergistics, blends, and multifunctional fertilizers are within the scope of the 4R management practices for adequate use of fertilizers (right source, right rate, right place, and right time).

The fertilizer technologies can reduce phosphorus losses in agricultural systems and lead to improvements in yield and quality of harvests. This increase in the efficiency of fertilization should always be linked with greater economic profitability and with less environmental impact, obeying the principles of sustainability and circular economy.

The big challenge for innovation is transforming the knowledge generated on present fertilizers into patents and scientific publications on technologies appropriate for the fertilizer market, and broadening access of consumers to this information.

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Dedication: I dedicate this article to the memory of ALFREDO SCHEID LOPES “ALFREDÃO”, one of the most incredible people I have had the opportunity of coming to know, a renowned professor with multiple skills and certainly one of the most important influential personalities on the world agriculture scene.

Abbreviations

DAP: diammonium phosphate; IFA: international fertilizer association; IFDC: international fertilizer development center; LDH: layered double hydroxides; MAP: monoammonium phosphate; MOF: metal-organic frameworks; NANO: nanoparticles; PCPF: polymer-coated phosphate fertilizers; SCMAP: elemental sulfur (S⁰)-coated MAP; SSP: single superphosphate; TNP: total neutralizing power; TSP: triple superphosphate; TVA: Tennessee Valley Authority.

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