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Preparation, forms and properties of controlled-release phosphate fertilizers

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Abstract

Controlled-release phosphate fertilizers include phosphate rocks (PRs) for direct application, partially acidulated phosphate rocks (PAPRs) and thermal phosphates. Phosphate rocks contain apatite as the main P containing mineral, the composition and the chemical nature of which vary between PRs. Based on the solubility in chemical extractants PRs are broadly grouped into 'reactive' and 'unreactive'. The 'reactivity' of PRs is influenced strongly by the extent of carbonate substitution for phosphate in the apatite minerals. Under certain soil and climatic conditions reactive PRs (RPRs) can be used as a source of P for direct application.

Partially acidulated phosphate rocks (PAPRs) are produced either by direct partial acidulation of PRs with mineral acids or by mixing PRs with fully acidulated superphosphate reaction mixtures. Partial acidulation of PRs with H_3PO_4 generally results in higher water soluble P contents than those acidulated with H_2SO_4. Mixing of RPRs with superphosphate reaction mixtures sometimes results in the preferential consumption of free acid and thereby increases the amounts of residual unreacted PRs.

Thermal phosphates are produced by either heating PRs below melting point both in the presence and the absence of silica (calcined phosphates) or heating PRs with silica above melting point (fused phosphate). These phosphates are alkaline in nature and hence suitable for acidic soils.

Introduction

Phosphate rocks (PRs) form the basic component from which all the phosphate fertilizers are produced (Fig. 1). Phosphate rocks are essentially insoluble in water (e.g. fluorapatite has a pk of 122.2) [36, 37] and need to be dissolved for the phosphorus (P) to become available to plants. Solubilisation of PRs in fertilizer manufacturing plants is achieved by wet process using mineral acids and by thermal treatment. Acid treatment results in either complete or partial dissolution of PRs depending on the amount and concentration of the acid used. Thermal treatment mostly results in partial decomposition of PRs. Complete dissolution of PRs results in water soluble phosphate fertilizers, whereas partial dissolution or decomposition results in phosphate fertilizer containing both water soluble and sparingly soluble P components.

Traditionally, most P has been applied to agricultural land in the form of water soluble fertilizers, such as single superphosphate (SSP), triple superphosphate (TSP) and diammonium phosphate (DAP). In recent years, however there has been renewed research interest in the use of controlled-release fertilizers which include RPR, for direct application and partially acidulated phosphate rock (PAPR) fertilizers. This change has been induced by several factors [4]: (a) PRs used for direct application and PAPR fertilizers have a higher P content than SSP

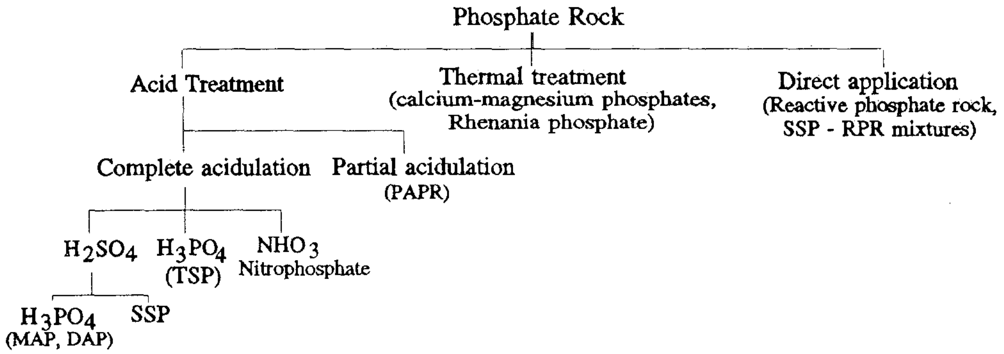

Fig. 1. Phosphate rock as a primary source of phosphate fertilizers.

making transport and spreading cheaper per unit P; (b) under certain soil, plant and climatic conditions RPRs and PAPR fertilizers have proved as effective as fully acidulated fertilizers; (c) in many countries price subsidies on manufactured phosphatic fertilizers have been removed forcing farmers to seek cheaper alternative fertilizers; (d) partial acidulation has proven to be an economically feasible method for improving the agronomic value of locally available PR materials of low chemical reactivity; (e) use of controlled-release phosphate fertilizers reduces leaching of P and subsequent eutrophication of water reserves; and (f) certain PR fertilizers have some liming action which can help to ameliorate soil acidity especially in soils with low buffering capacities.

The overall effectiveness of controlled-release phosphate fertilizers depends on the chemical and physical characteristics of these materials, the characteristics of the soils and the nature of the plant species. In this review the forms and characteristics of controlled-release P fertilizers are discussed.

Forms of controlled-release phosphate fertilizers

Controlled-release phosphate fertilizers are grouped into 3 broad categories. These include:

i) Reactive phosphate rocks (RPR) for direct application;
ii) Partially acidulated phosphate rocks (PAPR); and
iii) Thermal phosphates

The properties and the manufacture of these fertilizers are discussed below.

Phosphate rocks for direct application

Occurrence

Phosphorus occurs in nature as various mineral deposits of PR. These mineral deposits include: apatite (calcium phosphate); crandallite (aluminium phosphate); and millisite (iron and aluminium phosphate) [40]. The most abundant of these three is apatite, the composition of which can vary from the mineral fluorapatite, $Ca_{10}(PO_4)_6F_2$, to hydroxy apatite $Ca_{10}(PO_4)_6(OH)_xF_{2-x}$ and minerals of francolite type, $Ca_{10-\alpha}[Na-Mg]_\alpha(PO_4)_{6-\beta}(CO_3)_\beta F_\gamma$ where α and γ are functions of β, and $\beta = 1.5$ in the most substituted form [47].

Phosphate minerals occur in various geological formations as igneous, sedimentary and metamorphic depositions [35, 46]. Other small phosphatic deposits are those that are usually derived from guano. Igneous rocks are formed by crystallisation of primary minerals from the hot molten magma. Three of the largest apatite deposits in the world are of igneous origin, namely the Khibina deposits on the Kola Peninsula of USSR, the deposits of Eastern Uganda, and the Palabora deposits in East Transvel of South Africa [22, 56]. These deposits presently yield about 15% of the world's phosphate production [48].

Sedimentary rocks contain significant amount of fossil (organic) apatites and two major types of sedimentary deposits have been identified [57]. The first type represents deposits formed by divergent upwelling and occurs mostly as palatal particles. The second type is formed on the continental shelves or in continental interiors in association with limestone, dolomite, shale and glauconitic sandstone. In contrast to the deposits of igneous origin, the principle phosphate mineral in sedimentary deposits is carbonate apatite found in a microcrystalline structure (0.02-0.2μm). About 80% of the world production of phosphate comes from those deposits of sedimentary origin.

Metamorphic rocks are transitional in chemical nature between igneous and sedimentary rocks which are formed mostly under low temperature and pressure. Phosphate rocks derived from guano are formed when the soluble P in guano is carried downwards and replaces or alters the underlying rock. Where the underlying rock is limestone or dolomite, a secondary deposit of Ca phosphate (apatite) is formed and where the underlying rock is volcanic or igneous, Fe or Al phosphates (crandallite or millisite) are formed.

Reactivity

Phosphate rocks differ widely in their chemical composition and the nature of principle phosphate mineral, apatite can vary. Among the chemical characteristics, the degree of carbonate substitution of phosphate in the apatite structure has been found to be very closely related to the "reactivity" of PRs. Substitution of a divalent planar carbonate group for a trivalent tetrahedral phosphate group creates a charge imbalance and a packing void, which weakens the crystal structure of apatite (See Hagin and Harrison, Sale and Mokwunye and Chien in this issue). As the number of moles of hydroxide or carbonate per mole of phosphate increases the standard free energy of reaction of the apatite with acidic solutions becomes more negative and dissolution rate increases [19]. These aspects have been throughly reviewed by Khasawneh and Doll [35] McClellan and Gremillon [46] and more recently by Sanyal and DeDatta [55]. The degree of carbonate substitution is considered to be one of the important factors which determine the solubility of apatite and rate of dissolution of PR in acid soils [16]. Working with both synthetic and natural fluorapatite, Lehr and McClellan [39] found that as the extent of carbonate substitution increases, the crystalline size of the apatite mineral decreases resulting in a decrease in mineral stability or conversely an increase in the chemical reactivity of the PR.

The chemical "reactivity" of PRs can be empirically assessed according to their solubility in selected chemical extractants. For example, solubility of PRs in 2% citric acid, 2% formic acid [20,21] and N neutral ammonium citrate [46] has been used in New Zealand, Europe and USA and Australia, respectively as a measure of the reactivity of PRs. Based on the extractability of P by these extractants, Syers *et al.* [60] have arranged PRs into different reactivity groups–Sechura, North Carolina, Gafsa and Arad PRs being most reactive whereas Nauru, Christmas Island and Duchess PRs are among the least reactive (Table 1).

Reactivity vs plant availability

It has now been established that as the degree of carbonate substitution increases so does the potential agronomic effectiveness of PR. For example Caro and Hill [16] found that the amount of "bound carbonate" in PR materials was closely correlated with their effectiveness as a P source. Similarly Chien and Hammond [20, 21] found that the agronomic effectiveness of PRs increased as the degree of carbonate substitution increased. Recently Bolan *et al.* [6] compiled the agronomic effectiveness of a range of PRs in New Zealand and observed that in general the effectiveness increased with increasing chemical reactivity as measured by the solubility in various extractants (Fig. 2). Rajan *et al.* [54] also observed that the agronomic effectiveness of a range of PRs increased with an increase in the reactivity, as indicated by the solubility in formic acid. EEC regulations stipulate that a PR to be suitable for direct application should have a minimum total P content of 11%, 55% of which should be soluble in 2% formic acid and 95% particle size be $<63\mu$m [1]. Some PRs which qualify by EEC standard for direct application are: Sechura, Gafsa and North Carolina.

Table 1. Total P and citric acid soluble P contents of some commercially available phosphate rock materials

Phosphate rock	Origin	Total P (% w/w)	Citric P* (% Total P)
Christmas Island A	Christmas Island	16.4	23
Christmas Island C	Christmas Island	11.6	19
Duchess	Australia	13.5	6
Nauru	Nauru	15.6	22
Central Florida	USA	14.6	20
Khouribga	Morocco	14.4	26
Jordan	Jordan	15.0	26
Youssafia	Morocco	13.8	27
Egyptian	Egypt	13.0	33
Arad	Israel	14.4	30
Moroccan	Morocco	14.0	32
Chatham Rise	New Zealand	9.0	23
Sechura	Peru	13.2	43
Gafsa	North Africa	13.0	33
North Carolina	USA	12.8	32

* citric P > 30% = reactive PR: < 30% = unreactive PR

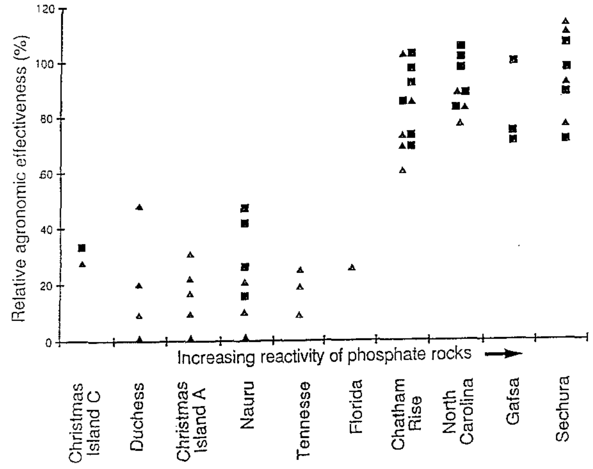

Fig. 2. Agronomic effectiveness of a range of phosphate rocks evaluated under glasshouse (▲) and field (■) conditions in New Zealand.

Apart from the composition of the apatite, PR particle size also determines PR reactivity in soils [61]. This is because PR dissolution is limited by the diffusion of dissolution products away from the PR surface. Grinding PRs to finer particle sizes provides an effective means of increasing the surface area at which dissolution occurs. Fineness of grinding will increase PR dissolution until the zone of dissolution around particles begins to overlap [36, 37].

The importance of removing the dissolution products from the site of dissolution can be manipulated to increase PR dissolution rates. For example, the agronomic effectiveness of PRs can be increased by adding an ion exchanger (such as ammonium -zeolite) which contains monovalent cations such as ammonium or potassium. The exchanger serves to sequester Ca^{2+} released from PRs, thereby shifting the equilibrium (Eq. 1) towards releasing more P to the soil solution [3].

$$\mathrm{PR} + \mathrm{NH_4\text{-}zeolite} \rightarrow \mathrm{Ca\text{-}Zeolite} + \mathrm{NH_4^+} + \mathrm{H_2PO_4^-} \quad (1)$$

Such fertilizers can provide a slow and sustained release of P. The rate of P and N (or K using K exchanger) release can be controlled by varying the PR/exchanger ratio [38]. Such mixtures are however expensive and remove the advantage of using PRs as low cost direct application fertilizers.

Granulation

Whereas the solubility of RPR and hence the P availability to crops increase with decrease in particle size, fine material is difficult to handle and spread giving problems with dustiness, material loss and segregation during transportation and application. Granulation of finely divided material can eliminate the dustiness but it can also cause reduction in the short-term P release [28]. With time however, as the plant root system develops and explore a large volume of fertilized zone, the effectiveness of the granules will become similar to the powdered ones [27]. The rates of release of P in granulated RPRs can be regulated by altering the size and the hardness of the granules.

Field trials on pasture have shown that there is no difference in pasture yield response to P between the ground RPR and the granulated form made with either bentonite [45] or with $MgSO_4.7H_2O$ [43]. The most suitable type of granules are those having good stability during handling but when applied to the soil should be easily broken down resulting in the dispersion of the particles.

Granulation techniques. Granulation of RPR is achieved either by wet granulation [15] or by dry compaction [44]. In both methods, small amounts of binding agents (2-5%) are generally added to improve the physical characteristics of the granules. The binding agents commonly used are: bentonite [45, 50], elemental sulphur (S°) [59], salts, such as KCl, $MgCl_2$, $MgSo_4$ [15, 27, 41] and $(NH_4)_2SO_4$ and urea [34] and mineral acids such as sulphuric, nitric, hydrochloride and phosphoric acids [58]. Of these binders, the mineral acids are considered to be the most promising as these not only produce granules with good physical characteristics due to the heat generated by the reaction of acid and RPR but produce small quantities of water soluble P.

Elemental sulphur too when incorporated in the molten stage to the RPR not only produce hard robust granules, but also gives a 'biosuper' effect [52, 59] of increasing the solubility of RPR by the reaction of the RPR with H_2SO_4 produced by the microbial oxidation of S° in the soil.

Use of salts has been successful especially in minigranulation of RPR [41, 50]. Of the various salts used, $MgSO_4.7H_2O$ appears to produce granules of high strength. Granulation of RPRs using salts requires drying for the salt crystals to form and bind the RPR particles thereby giving strength to the granules.

Use of ammonium salts and urea in RPR granulation increases the solubility of RPR by the action of acid generated through nitrification of the ammonium ions [34]. For this effect to be significant the N/P ratios need to be high and this is practical only when both N and P fertilizers are required for the crop. The strength and critical relative humidity of these granules may not be sufficiently high to withstand granule degradation and caking on storage and transportation.

Measurement of granule solubility. The ability of RPR particles to release soluble P to soil is determined in the laboratory by shaking the RPR with weak acids or salts (citric and formic acids and ammonium citrate) and measuring the soluble P (See Chien in this issue). These methods are not suitable for determining the agronomic value of granulated RPR as the granules would disintegrate on shaking with the extractants. Chien and Hammond [20] developed a non-shaking method where the granules are mixed with a H-resin and sand and the P released is measured after 6 days. The H-resin provides a sink for the Ca^{2+} released from the RPR as well as provides H^+ for the dissolution of RPR. Using this method, Chien and Hammond [20] observed that P solubility decreased with an increase in granule size whereas the solubility of P was same for all granule sizes when the conventional ammonium citrate method was used. Crop yields were highly correlated with P extracted by H-resin method but not with citrate method. Gillon and Hagin [26] used a similar method except they provided an additional anion resin as a sink for dissolved P and obtained similar results as Chien and Hammond [20].

Partially acidulated phosphate fertilizers

Fully acidulated phosphate fertilizers, such as SSP, TSP and nitrophosphates are produced by complete (100%) acidulation of PRs with mineral acids such as sulphuric (H_2SO_4), phosphoric

(H_3PO_4), or nitric (HNO_3) acids, based on the stoichiometric reaction between apatite in PR and acid. Partially acidulated phosphate rock (PAPR) fertilizers are produced by two processes: (1) by direct acidulation of PRs with less acid than that required for complete acidulation (i.e. directly acidulated PAPR); and (2) by indirectly mixing different proportions of fully acidulated fertilizers and unacidulated PRs (i.e. superphosphate: phosphate rock mixtures). Some of the PAPR fertilizers that are commercially available are given in Table 2.

Method of manufacture

The manufacture of both directly acidulated PAPR and superphosphate: phosphate rock mixtures involves the acidulation of PRs with mineral acids. To understand the reactions occurring during the manufacture of these fertilizers, it is necessary to examine the reactions that occur during the manufacture of a fully acidulated phosphate fertilizer such as SSP or TSP. In SSP production H_2SO_4 reacts with part of the PR component to produce H_3PO_4 (Eq. 2) which subsequently reacts with the remaining (unacidulated) PR to produce monocalcium phosphate (MCP)(Eq. 3). TSP is manufactured by acidulating PRs with H_3PO_4 and therefore only the second reaction (Eq. 3) occurs.

$$\begin{aligned}&2Ca_{10}(PO_4)_6F_2 + 9H_2SO_4 \rightarrow 9CaSO_4\\&\quad + 6H_3PO_4 + CaF_2 + Ca_{10}(PO_4)_6F_2\end{aligned} \tag{2}$$

$$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + 12H_3PO_4 \rightarrow 9Ca(H_2PO_4)_2\\&\quad + CaF_2\end{aligned} \tag{3}$$

Both SSP and TSP contain mostly MCP and small amounts (5-15%) of unacidulated PR as the P components. In SSP production considerable amounts of gypsum ($CaSO_4.2H_2O$) are also formed; this product is only a trace impurity in TSP due to the presence of small quantities of residual H_2SO_4 in commercial H_3PO_4.

Directly acidulated PAPR

Manufacture. The nominal percentage of partial acidulation is calculated from the amount of acid used expressed as a percentage of the amount of acid required for complete acidulation of the PR. Braithwaite [8] summarised the reaction of different acid combinations and acid to rock ratios by the following idealized equation:

$$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + y(6-x)H_2SO_4\\&\quad + 2xyH_3PO_4 \xrightarrow{H_2O} y(6-x)CaSO_4\\&\quad + (3+x)yCa(H_2PO_4)_2H_2O\\&\quad + (1-y)Ca_{10}(PO_4)_6F_2 + yCaF_2\end{aligned} \tag{4}$$

Table 2. Phosphorus contents (% w/w) of a range of partially acidulated and thermally treated phosphate fertilizers

Products	Origin	Total P (% w/w)	Remarks
Directly acidulated PAPRs			
ESPARP	Australia	10.1	Duchess PR + H_2SO_4 + S°
Granphos	United Kingdom	16.4	Gafsa PR + H_3PO_4 + $NH_4H_2PO_4$
Hyphos	New Zealand	16.0	NCPR + H_3PO_4
Hyphos S	New Zealand	15.0	NCPR + H_3PO_4 + S°
Novaphos	Germany	–	
Single superphosphate-reactive phosphate rock mixtures			
Coastal super	Australia	9.5	SSP + NCPR + S°
Endurophos	New Zealand	10.8	SSP + NCPR
Longlife	New Zealand	10.8	SSP + NCPR
Longerlife	New Zealand	10.8	SSP + NCPR
Fused phosphates			
Basic slag	Germany	8.1	Byproduct
Fused magnesium phosphate	Japan	10.3	Florida PR
Fused defluorinated phospate	Brazil	12.5	Araxia PR
Calcined phosphates			
Rhenania phosphate	Germany	12.7	PR + Na_2CO_3 + silica
Calciphos	Australia	13.0	Xmas C grade PR

where y = acidulation factor and x = acid selection factor

when	$y = 1, x = 0$	Single superphosphate
when	$y = 1, x = 6$	Triple superphosphate
when	$0 < y \leq 0.75$	PAPR
when	$0 < y \leq 0.75$, $6 > x > 0$	Mixed acid PAPR

The most important products formed during the manufacture of PAPRs are $CaSO_4.H_2O$, MCP and residual PR, if H_2SO_4 or mixed acid is used and MCP and residual PR, if H_3PO_4 is used alone. Phosphoric acid acidulated PAPRs contain only minimal amounts (<2%) of sulphur [10, 11]. Sulphur in the form of sulphate can be provided in a PAPR by using H_2SO_4 or mixed acid (H_3PO_4 plus H_2SO_4) for acidulation but to maintain high P analysis S° can be incorporated into PAPRs (Table 2). This is achieved by either adding the molten S° in the H_3PO_4 prior to the addition of acid to the rock or adding S° immediately after the hot H_3PO_4 and PRs are mixed [17]. These methods lead to finely divided S° (approximately 75% < 250μm) being incorporated evenly through the granule.

Granulation. Under laboratory conditions good PAPR granules have been obtained by granulating immediately after denning [25, 53]. Good granulation could also be achieved using direct acidulation–granulation techniques. The latter method involves spraying the H_3PO_4 onto a PR sample rotating on a pan or a drum. Using this technique Braithwaite and Rogers [13] have achieved a good granulation for medium fine (60% < 150μm) or finely ground (70% < 75μm) North Carolina PR (NCPR) with both technical grade and works-grade H_3PO_4, but for unground PR only technical grade acid produced good granules. Under commercial conditions, however, it is difficult to achieve one step acidulation, granulation and drying and requires stockpiling the ex-den material for an extended period to obtain granules robust enough to withstand the drying process.

Granulation of PAPR was found to be less affected by the type of RPR than by the type and concentration of acid used. For both mixed acid or H_3PO_4 acidulation the nature of the H_3PO_4 can affect the rate of reaction, the chemical analysis, and the quality of granules produced [14]. The presence of Fe, Al and Mg impurities causes a retardation of the reaction rate while usually improving granules strength [9]. Hedley *et al.* [32] examined the effect of acid concentration on the granulation of PAPR. Amongst the three acid concentrations tested (50%, 52% and 55% H_3PO_4) they observed that the highest granule strength was obtained at the lowest concentration of H_3PO_4 and related the effect of acid concentration on granulation to the amount of moisture and free acid present in the reaction mixture. It was assumed that the moist and heavier reaction mixtures generated more mechanical energy in the granulation drum.

Superphosphate-phosphate rock mixtures

Manufacture. Superphosphate-phosphate rock mixtures are manufactured either by dry bulk blending of the granulated SSP (or TSP) and as received PR [49], or by adding RPR to an ex-den SSP reaction mixture (SSP-RPR) which is subsequently granulated [12]. In the first process, simple batch blending leads to fertilizer segregation on transport and spreading because of the contrasting particle size of the two components. Commercial SSP-RPR mixtures are manufactured by adding unground RPR such as NCPR to immature ex-den SSP made from less reactive PRs [12].

The overall chemical reactions which occur during the manufacture of SSP-RPR can be approximated as follows [10]:

$$\begin{aligned} &3PR + 18H_2SO_4 \rightarrow 4.5MCP + 18CaSO_4 \\ &+ 2.5CaF_2 + PR + 6H_3PO_4 + \xrightarrow{4RPR} 9MCP \\ &+ 18CaSO_4 + 3CaF_2 + PR + 3RPR \qquad (5) \end{aligned}$$

Granulation. The addition of RPR to ex-den wet SSP reaction mixture was found to be a suitable way for granulating RPR. In commercial plants, however, unless these two components are thoroughly mixed segregation occurs during granulation. Recent study by Braithwaite *et al.* [14] has indicated that more non-uniform mixing occurs in SSP-RPR mixtures than in directly acidulated PAPR. In the case of SSP-RPR, the total P content was higher in <1 mm sized granules than >1 mm sized granules suggesting that most of the RPR added at ex-den stage was not uniformly mixed with SSP.

Characteristics of PAPR

The agronomic value of directly acidulated PAPRs and SSP-RPR moistures is influenced by both their water soluble P content and the chemical nature of the non-water soluble P residue, which includes secondary P products, such as DCP and unacidulated PR. Therefore in terms of measuring the chemical quality of these products it is usual to measure their solubility in water or neutral ammonium citrate (NAC) and the solubility of the water-insoluble residue in either 2% formic or citric acids. The solubility characteristics of these fertilizers are affected by manufacturing variables [4].

Directly acidulated PAPR

Solubility. In the case of H_3PO_4 acidulated PAPRs, most of the soluble P is contributed by the acid, whereas in the case of H_2SO_4 acidulated PAPRs, soluble P is contributed solely by the PRs. This suggests that the soluble P content of the former PAPRs is mainly determined by the quality of the acid but that of the latter, by the quality of the PRs. For the same level of nominal acidulation, H_3PO_4 acidulation yields higher P analysis fertilizers, with a higher water soluble P content than does H_2SO_4 acidulation.

H_2SO_4 can easily be produced in a pure form from elemental sulphur; whereas, commercial grade H_3PO_4 made from full acidulation of PR with H_2SO_4 is often contaminated with small amounts of residual H_2SO_4 and various soluble ions ("gangue" materials) originating from the PR [24]. Braithwaite [9] has shown that the presence of Fe, Al and Mg ions in commercial H_3PO_4 acid greatly reduced the rate of PR acidulation. A ranking of acid quality can be obtained by calculating the amount of PR-P converted to soluble P per unit of acid P added. On this basis, Harrison and Hedley [30] have shown that the total Fe and Al content of the acid strongly influences acid quality and subsequent conversion of PR-P to soluble P.

When a range of PRs were acidulated with H_3PO_4 on a per unit of apatite P basis, Harrison and Hedley [30] observed that there was little effect of the nature of the apatite on the water soluble P content of the product. However, secondary minerals such as free carbonate present in a PR influence the water soluble P content of the product by neutralising some of the acid added. When PRs are acidulated with H_2SO_4, gangue materials present in the PRs significantly influence the water solubility of the PAPR product and the solubility of the unacidulated PR residue. For example, Hammond *et al.* [29] have observed that both the water soluble P and the agronomic effectiveness of PAPRs decrease with increasing content of Fe and Al oxides in the PRs. The effect was more pronounced at higher level of acidulation, presumably because more Fe and Al oxides were solubilized and reacted with water soluble P to form water insoluble Fe and Al phosphates.

Deactivation. It has often been observed that the formic citric solubility of the non-water soluble residues of PAPR are in general lower than the original PRs. This decrease in solubility of the residual PR ("deactivation") has generally been related to the selective dissolution of a more soluble fraction of PRs during the manufacture of PAPR or that a coating of less soluble material is formed over the original PR [18] (See also Rajan and Marwaha, in this issue). Hedley and Rowarth [33] have shown that the residual PR originating from PAPR and RPR directly added to soil had similar solubility. Thus from an agronomic standpoint partial acidulation of RPR (PAPR) may not devalue the effectiveness of residual RPR.

Single superphosphate-reactive phosphate rock mixtures

Similar to directly acidulated PAPRs, the water solubility of the SSP-RPR mixture is dependent upon the degree of acidulation of the PR used for SSP production and the amount of RPR added ex-den. Again factors, such as the amounts of gangue material in both PRs influence the extent of water soluble P production and the solubility of the unacidulated residues. Also during the manufacture of these mixtures, addition of RPR to immature exden SSP reaction mixtures may result in an interaction between these two components.

Solubility. The amount of PR residue remaining in a SSP-RPR mixture and the solubility of the product depend on the type of PR used for SSP, type of RPR and the time of addition of RPR to ex-den SSP reaction mixture.

The extent of acidulation of the RPR when mixed with SSP reaction mixture is determined by the nature and amount of free acid remaining in the SSP reaction mixture, which in turn is affected by the type of PR used for SSP manufacture. Hedley *et al.* [31] have observed that among several PRs used for SSP manufacture, free acid in a SSP mixture made from Christmas Island A grade rock (Xmas) contained the highest amounts of Fe and Al and was less effective in converting P in RPR (added exden) to soluble P. As a consequence, the presence of Xmas PR in the SSP-RPR reaction mixture decreases the amount of acidulated P in the SSP-RPR mixtures.

The nature of RPR added had a significant effect on the solubility of P in SSP-RPR mixtures [31]. For example, SSP-RPR moistures with unground NCPR or ground Jordan PR had similar solubilities in water and neutral ammonium citrate, but had significantly lower solubilities in 2% citric and formic acids than when ground NCPR was added. Hedley *et al.* [31] demonstrated that although the initial acidulation of PR increased with time of acidulation, provided the RPR is not added within 20 minutes of acidulation, the time of addition of RPR has no significant effect on the solubility of P in the SSP-RPR mixtures.

The interaction between SSP reaction mixture and ex-den reactive phosphate rock. During the manufacture of SSP-RPR mixtures RPR is likely to react with free H_3PO_4 remaining in ex-den reaction mixture in preference to the unreacted PRs resulting in a decrease in citric solubility of SSP-RPR mixtures [12]. Evidence for the preferential consumption of free acid by RPR was obtained from a study by Bolan *et al.* [5]. At the ex-den stage, immediately prior to the addition of NCPR, the amount of free acid in the SSP reaction mixture was 12–15%, which decreased to <6% with the addition of NCPR. Hedley et al. [31] observed that the rate of free acid consumption by the RPR is 10 to 100 times faster than that by the partially acidulated residual PR in the mixture. The preferential consumption of free acid may be due to the higher reactivity and unacidulated surface of the RPR compared to the partially acidulated PR which may be coated with gypsum [12].

Preferential consumption of free acid by RPR essentially stops the further acidulation of the partially acidulated PR residues resulting in more residual PR in SSP-RPR mixtures than in straight SSP. In a laboratory study Bolan *et al.* [5] have shown that the amount of unacidulated Nauru and Xmas PRs were 15 and 42%, respectively in straight SSP which increased to 32 and 48% in SSP-RPR mixtures. In a commercial production, however, Loganathan and Hedley [42] have shown that the amount of unreacted Nauru and NCPR from a feed rock blend of these two PRs were 3.5% and 2.8%, respectively in SSP and 5.7% and 2.4% in SSP-RPR mixture. Results from Bolan *et al.* [5] have established that the less mature the SSP is when the RPR is added, the more unreacted PR residue remains in the product.

Thermally treated phosphates

Thermally treated phosphates are grouped into fused and calcined phosphates [2] (Table 2). Fused phosphates are obtained by heating PRs and silica mixtures to above melting point. Calcined phosphates are produced by heating PRs either in the presence or absence of silica to below the melting point. Thermal phosphates are generally alkaline in nature containing large amounts of Ca with either Mg or Na and are therefore suitable for acidic soils. The common characteristics of thermal phosphates is that they require high energy input for calcination or fusion. The increase in energy cost has made these phosphate fertilizers more expensive than wet process PR solubilization. Nevertheless, some igneous PR which are unsuitable for wet process can be decomposed by the thermal treatments.

Fused phosphate

The most commonly used fused phosphates is fused magnesium phosphate (FMP). FMP is produced by fusion of a mixture of PR and magnesium silicates, such as serpentine and olivine. The mixture is fused at 1300 to 1500 °C in an electric furnace or open hearth furnace and quenched by water to give a vitreous product. The solubility of FMP increases with increasing temperature of fusion. Florida PR and Araxia PR have been used to produce FMP in Japan and Brazil, respectively. FMP containing micronutrients have been produced commercially in Japan.

Calcined phosphates

The most commonly used calcined phosphates are Rhenania phosphates and defluorinated phosphate. Rhenania phosphate is produced in Germany by calcining a blend of PR, sodium carbonate and silica (10:3.5:1.0) at 1200 °C to 1300 °C.

$$Ca_{10}(PO_4)_6F_2 + 4Na_2CO_3 + 2SiO_2 \rightarrow \underset{\text{Rhenanit}}{\underline{6CaNaPO_4}} + 2CaSiO_4 + 2NaF + 4CO_2 \qquad (6)$$

Deflourinated phosphates are obtained by calcining PR at 1400 °C with silica in the presence of steam. The phosphate produced by this process in UK is called 'silicophosphate'. Defluorination can also be achieved by calcination of PR with a small amount of H_3PO_4.

$$2Ca_{10}(PO_4)_6F_2 + SiO_2 + 2H_2O \rightarrow 6Ca_3(PO_4)_2 + CaSiO_4 + 2HF \qquad (7)$$

Production of calcined phosphate using the C grade Christmas Island PR has been extensively researched by the British Phosphate Commission. The C grade ore contains 11.9% P and is high in iron (11% Fe_2O_3) and aluminium (24% Al_2O_3). In the commercial operation the C grade ore is heated at about 550 °C in a submerged combustion calciner where dehydroxylation reaction renders the insoluble C grade ore partially soluble. Unlike fused phosphates, these products reach a maximum solubility at about 500 °C. Palmer [51] has shown that the calcium aluminium phosphate compounds present in C grade ore (millisite and crandallite) are completely altered to amorphous phase at 350 °C to 500 °C. Further increase in the calcination temperature results in the recrystallisation of Ca phosphate (Whitlockite) and Al-phosphate (phosphocristobalite) and thereby decreases the solubility.

In a continuous flow calciner the ununiform distribution of temperature results in products with a range of solubility. Fine fractions elutriated in the upwards gas discharge are collected and marketed as "Citraphos" whereas the coarse material in the underflow is finely ground and marketed as 'calciphos'. Large number of glasshouse and field experiments have been carried in Australia and New Zealand evaluating the suitability of these products as slow release fertilizers [7, 23].

Conclusions

Controlled release P fertilizers such as RPR, PAPR and SSP-RPR have largely arisen as low cost alternatives to fully acidulated fertilizers or thermal phosphates have been manufactured when the nature of accessory minerals in the apatite makes acidulation inefficient. Only RPRs which dissolve readily in soils are considered to be suitable for direct application. The more reactive phosphate rocks are of sedimentary origin. The reactivity of a PRs is influenced strongly by the extent of carbonate substitution for phosphate in the apatite crystal. Manufacture and use of PAPRs is aimed at improving the agronomic value of indigenous PRs, to produce a partially soluble low-cost high analysis P fertilizers and to achieve granulation of RPRs. PAPRs are produced either by direct acidulation of PRs or by mixing fully acidulated phosphate fertilizers with RPRs. The solubility of PAPRs is determined by the quality of both the PRs and the acid used for acidulation.

Thermal phosphates are produced by high temperature heat treatment of PRs. The high energy consumption during the manufacture of these products makes them expensive forms of P fertilizer.

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