

Chapter 11

Legislation and quality control of phosphate rocks for direct application

Many countries, especially developing countries, have legislation to ensure that the physical and chemical qualities of commercial fertilizers meet the specifications set by the governments in order to safeguard consumers' interests. However, in some developed countries, e.g. the United States of America, it is possible to sell fertilizers without specifications provided they meet the 'truth in labelling' requirement.

In 1998, the consumption of direct application phosphate rock (DAPR) represented less than 2 percent of world P_2O_5 consumption (Maene, 2003). The information available in literature on the legislation for phosphate rock (PR) as a fertilizer for direct application is similarly limited. This chapter reviews some of the existing legislation in various countries concerning DAPR. It then discusses issues associated with the legislation and recommends legislation guidelines for the quality control of DAPR.

CURRENT LEGISLATION ON PHOSPHATE ROCK FOR DIRECT APPLICATION

Most legislation concerning PR for direct application includes three main specifications: total P_2O_5 content of PR, chemical property (solubility), and physical property (particle size). The following sections present examples of legislation adopted in countries that use DAPR.

In 1976, the Council of the European Communities (EC) issued a directive (Official Journal of the European Communities, 1976) regarding the specifications of DAPR as follows: (i) minimum 25 percent total P_2O_5 ; (ii) at least 55 percent of total P_2O_5 soluble in 2-percent formic acid (FA); and (iii) at least 90 percent through 0.063 mm (250 Tyler mesh) and 99 percent through 0.125 mm (115 Tyler mesh) in particle-size distribution.

In Malaysia, PR has been in widespread use since the 1950s for plantation crops (e.g. oil-palm and rubber). In 2000, Malaysia imported almost 500 000 tonnes of various PR sources. In 1998, the Department of Standards of Malaysia revised the previous 1972 specifications as follows: (i) minimum 28 percent total P_2O_5 ; (ii) at least 7.5 percent P_2O_5 (weight basis) soluble in 2-percent citric acid (CA); and (iii) 90 percent less than 0.500 mm (32 mesh) in particle-size distribution (Malaysian Standard, 1998). Thus, the unground, as-received PRs can now meet the particle-size requirement stipulated by legislation in Malaysia.

In Brazil, the use of imported, unground, as-received, highly reactive PRs, e.g. Gafsa (Tunisia), Arad (Israel), Daoui (Morocco) and Djebel Onk (Algeria), increased sharply to about 320 000 tonnes in 2000 (ANDA, 2001). The Brazilian Ministry of Agriculture publishes the regulations for "as-received, natural reactive phosphate" (Regulations Nos. 9, 63, 161 and 19). These specify: (i) minimum 28 percent of total P_2O_5 ; (ii) at least 9 percent P_2O_5 (weight basis) soluble in 2-percent CA; (iii) 100 percent less than 4 mesh (4.8 mm) and 80 percent less

than 7 mesh (2.8 mm) with a tolerance of 15 percent for particles larger than 4.8 mm; and (iv) calcium (Ca) content of 30–35 percent.

In India, the consumption of PRs, mainly indigenous low reactive and low grade for direct application, was about 25 000 tonnes as P_2O_5 in 1998 (Maene, 2003). Imports of PR are subject to an import duty of 5 percent. The Indian Fertilizer (Control) Order issued in 1985 for PR is: (i) minimum 18 percent of total P_2O_5 ; and (ii) 90 percent less than 100 mesh (0.15 mm) and the remaining 10 percent must be less than 60 mesh (0.25 mm). There is no minimum solubility requirement of PR in the legislation.

In New Zealand, the use of imported, reactive PRs for direct application increased from 102 000 tonnes in 1996 to 130 000 tonnes in 2000, about 10 percent of all phosphorus (P) products sold on both a tonnage and dollar basis (Quin and Scott, 2003). In New Zealand and Australia, there is no legislation on DAPR. In general, reactive PR is defined as 30 percent of total P_2O_5 being soluble in 2-percent CA under standard conditions (Quin and Scott, 2003; Hedley and Bolan, 2003). Compared with 2-percent CA and neutral ammonium citrate (NAC), the 2-percent FA test best predicts the agronomic effectiveness of PRs varying in reactivity and particle size (Hedley and Bolan, 2003; Bolland and Gilkes, 1997). However, 2-percent CA remains the standard test in New Zealand and Australia.

ASSOCIATED ISSUES

The main factors affecting the agronomic effectiveness of DAPR: (i) inherent PR properties; (ii) type of soil; (iii) crop species; (iv) management practices; and (v) agroclimatic conditions (Chien and Menon, 1995b; Hammond *et al.*, 1986b; Khasawneh and Doll, 1978; Rajan *et al.*, 1996). Chapter 5 provides more details on these aspects.

All regulations concerning DAPR focus on the quality control of different PR sources, namely: (i) total P_2O_5 content; (ii) PR solubility; and (iii) particle-size distribution of PR. Thus, there is a need to discuss the issues of these physical and chemical properties of PR associated with legislation for DAPR.

Total P_2O_5 content of PR

TABLE 35
Total P_2O_5 , NAC-soluble P_2O_5 , and $CO_3:PO_4$ ratio of apatite in various phosphate rocks

PR source ^a	$CO_3:PO_4$	Total P_2O_5 (% of rock)	NAC- P_2O_5 ^b
North Carolina, United States of America	0.26	30.0	7.6
Arad, Israel	0.20	32.4	7.1
El-Hassa, Jordan	0.16	31.3	5.8
Hahotoe, Togo	0.11	36.8	3.9
Idaho, United States of America	0.08	32.3	3.5
Kaiyang, China	0.05	17.6	3.4
Araxa, Brazil	< 0.01	36.1	2.8
Dorowa, Zimbabwe	< 0.01	33.1	1.9
Sukulu Hills, Uganda	< 0.01	41.0	1.6

a. Ground to minus 100-mesh (0.15 mm) size.

b. NAC, second extraction.

The total P_2O_5 content of a PR bears no relationship to its chemical reactivity and agronomic effectiveness. In fact, a PR with a very high total P_2O_5 content (33–40 percent) may indicate that the PR is potentially low in chemical reactivity. As more CO_3 substitution for PO_4 in an apatite structure results in a lower total P_2O_5 content and higher chemical reactivity, a very high total P_2O_5 content suggests that the apatites in the PR have very low CO_3 substitution in the apatite structure and, hence, low chemical reactivity

(Rajan *et al.*, 1996). Table 35 presents data on some PRs that vary widely in the $\text{CO}_3:\text{PO}_4$ ratio of apatite, total P_2O_5 content, and solubility in NAC solution. The solubility is related closely to the $\text{CO}_3:\text{PO}_4$ ratio of apatite but not to the total P_2O_5 content. Therefore, the inclusion of a minimum total P_2O_5 content in legislation should be based not on agronomic considerations but only on the consideration of protecting PR users from unscrupulous suppliers.

SOLUBILITY OF PHOSPHATE ROCK

The agronomic effectiveness of PR depends considerably on its chemical reactivity. This is determined conventionally by measuring the solubility of the PR in extracting solutions. The three most commonly used extraction methods (Chien and Hammond, 1978) are:

- NAC: A 1-g sample of PR is extracted with 100 ml of NAC solution at 65 °C for 1 h. This method is used mainly in the United States of America.
- 2-percent CA: A 1-g sample of PR is extracted with 100 ml of 2-percent CA at room temperature for 1 h. This is probably the most common method of the three in countries where PR has been used, e.g. Malaysia, Brazil and New Zealand.
- 2-percent FA: A 1-g sample of PR is extracted with 100 ml of 2-percent FA at room temperature for 1 h. This method is used in countries of the EC.

Although a given method specifies the extracting conditions such as solid-solution ratio, temperature, and time of extraction, there are no specifications on other conditions that may affect the solubility measurement, e.g. types of shaking apparatus (horizontal shaker, wrist-action shaker, reciprocal shaker, magnetic stirring bar, etc.), shaking or stirring speed during extraction, and size of shaking flasks used. Therefore, there is no universal method for measuring PR solubility.

However, even if a method did specify all the conditions for measuring PR solubility, there are other issues that would affect measurements.

Expressing PR solubility

The solubility of PR is commonly expressed as a percentage of total P_2O_5 . For example, a PR has 30 percent total P_2O_5 , and the NAC-soluble P_2O_5 is 6 percent when a 1-g sample is extracted with 100 ml of solution. The solubility of the PR is then expressed as 20 percent of total P_2O_5 in NAC. However, when comparing the solubility of PR sources that vary widely in total P_2O_5 content, the solubility is expressed more appropriately as a percentage of rock (weight basis) (Chien and Hammond, 1978; Chien, 1993, 1995). The expression ‘percentage of total P_2O_5 ’ may give a misleading comparison when PR sources containing low total P_2O_5 content are used. Table 36 shows this P_2O_5 -grade effect. The NAC solubility expressed as a percentage of PR and sand mixture was relatively constant (5.5–6.0 percent) down through the 50:50 PR-sand mixture. On the other hand, citrate solubility expressed as a percentage of total P_2O_5 increased from 21.0 to 61.8 percent when total P_2O_5 of PR was diluted from 27.2 to 7.6 percent. The constant citrate solubility expressed as percentage of mixture was due to the fact that the solubility of a given apatite is fixed by its solubility-product constant (Chien and Black, 1976).

In a study to compare various laboratory methods for predicting the agronomic potential of DAPRs, Chien and Hammond (1978) observed that the solubility of two low-grade PRs (Pesca and Huila) appeared to increase with respect to other sources when the solubility was expressed

TABLE 36
Citrate solubility of mixtures of North Carolina PR and sand

Composition of mixture		Total P ₂ O ₅ content	Neutral ammonium citrate solubility	
PR	Sand		of mixture	of total P ₂ O ₅
%				
0.91	0.09	27.2	5.7	21.0
0.86	0.14	25.7	5.9	23.0
0.80	0.20	23.9	6.0	25.1
0.69	0.31	20.6	5.6	27.2
0.65	0.35	19.4	5.7	29.4
0.50	0.50	14.9	5.5	36.9
0.25	0.75	7.6	4.0	61.8

Source: Lehr and McClellan, 1972.

TABLE 37
Citrate solubility of PRs containing various amounts of total P₂O₅ content

PR source	Total P ₂ O ₅ content	Neutral ammonium citrate solubility	
		of rock	% of total P ₂ O ₅
%			
Huila, Colombia	20.9	3.5	16.2
Pesca, Colombia	19.8	1.8	9.5
Sechura, Peru	29.9	5.3	18.0
Gafsa, Tunisia	29.9	5.5	18.6
North Carolina, United States of America	30.0	6.7	22.4
Central Florida, United States of America	32.7	3.2	9.7
Tennessee, United States of America	30.1	2.8	8.9

Source: Chien and Hammond, 1978.

as a percentage of total P₂O₅ rather than as a percentage of rock (Table 37). For example, Huila PR and Central Florida PR had about the same citrate solubility expressed as a percentage of rock. When the solubility was expressed as percentage of total P₂O₅, Huila PR appeared to have a higher solubility than Central Florida PR. Braithwaite *et al.* (1989, 1990) also reported that the total P₂O₅ content of PR affected its solubility as measured by 2-percent CA and 2-percent FA; when a 1-g sample of any PR was used for assessment, PRs with a lower P₂O₅ content had an advantage over PRs with higher total P₂O₅ content.

Therefore, it appears that PR solubility expressed as percentage of rock rather than as percentage of total P₂O₅ provides a more accurate assessment when comparing the solubility of PR sources that vary widely in total P₂O₅ content.

Free carbonate effect

It is the apatite-bound carbonate and not the total carbonate (which may also contain free carbonates, such as calcite and dolomite, as accessory minerals in PR) that determines the solubility of PR. The presence of free carbonates in a significant amount can suppress the solubility of the PR. The apparent decrease in the solubility of apatite is due to the Ca-commonion effect and consumption of extracting solutions, which occur because free carbonates are more soluble than apatite.

Chien and Hammond (1978) measured the reactivity of seven PRs by various chemical extractions (Table 38). The P solubility in NAC remained relatively constant between the first and second extractions for each PR except Huila PR. The Huila PR contains about 10 percent free CaCO₃ that suppressed the apatite solubility during the first extraction but not during the

TABLE 38
Solubility of PRs as measured by various chemical extractions

PR source	Soluble P ₂ O ₅ , % of rock			
	Neutral ammonium citrate		2% citric acid	2% formic acid
	1st extraction	2nd extraction		
Huila, Colombia	0.9	3.5	5.3	6.2
Pesca, Colombia	1.8	1.8	6.9	5.3
Sechura, Peru	5.3	5.3	15.2	21.9
Gafsa, Tunisia	4.8	5.5	14.0	22.3
North Carolina, United States of America	7.1	6.7	15.9	25.8
Central Florida, United States of America	3.0	3.2	8.5	8.3
Tennessee, United States of America	2.5	2.8	8.7	6.9

Source: Chien and Hammond, 1978.

second extraction. MacKay *et al.*, 1984 also found that the citrate-soluble P₂O₅ of Chatham Rise PR (New Zealand), which contains 27.6 percent free CaCO₃, increased from 3.2 percent in the first extraction to 10.1 percent in the second extraction.

The data in Table 38 indicate that the solubility of Huila PR was still suppressed by the free CaCO₃ in the PR as measured by 2-percent CA and 2-percent FA when comparing the solubility of Huila PR and Central Florida PR in the second extraction with NAC. However, the degree to which the free CaCO₃ affected the solubility of Huila PR appeared to decrease as the strength of the extracting solution increased from NAC to 2-percent CA and to 2-percent FA. To measure the actual solubility of a PR, a second extraction with NAC and 2-percent CA is therefore recommended when comparing the solubility of PR sources containing various amounts of free carbonates. For 2-percent FA, one extraction may suffice if the PR does not contain a significant amount of free CaCO₃.

Particle-size effect

The solubility of PR increases with decreasing particle size (Chien, 1993, 1995). However, a very fine grinding of a low-reactivity PR cannot increase its solubility significantly enough to compensate for the nature of its low reactivity owing to low CO₃ substitution for PO₄ in the apatite structure. Table 39 shows that the solubility of finely ground low-reactivity PRs is still lower than unground, as-received, high-reactivity PRs. The solubility of finely ground, highly reactive North Carolina PR was significantly higher than its unground form (Table 39). However, there were reportedly no significant differences in agronomic effectiveness obtained with finely

TABLE 39
Solubility of ground and unground PRs

PR source ^a	Soluble P ₂ O ₅ , % of rock	
	Neutral ammonium citrate	2% citric acid
Gafsa (Tunisia), unground	6.3	10.6
North Carolina (United States of America), unground	6.4	10.6
North Carolina (United States of America), ground	7.1	15.9
Hahotoe (Togo), ground	4.1	7.6
Kaiyang (China), ground	3.4	7.2
Araxa (Brazil), ground	2.8	5.0
Jhamarkotra (India), ground	0.6	1.5

a. Unground = 95% < 32 mesh (0.50 mm); ground = 100% < 100 mesh (0.15 mm).

ground and unground forms for highly reactive PRs, e.g. North Carolina (Chien and Friesen, 1992) and Gafsa (Chien, 1998). Thus, it is not necessary to grind highly reactive PRs finely for direct application. Indeed, several highly reactive PRs for agronomic use are in unground, as-received forms, e.g. Gafsa PR (Tunisia), Djebel Onk PR (Algeria), and Sechura PR (Peru). The use of unground PRs for direct application saves on grinding cost and also reduces the dustiness of PR during handling and application.

As the agronomic effectiveness of PR depends on its solubility rather than particle size, the regulations regarding DAPR should not require all PRs, including the highly reactive types, to be ground to less than 100 mesh (0.15 mm). The minimum solubility requirement should be based on the PR products actually used, be they ground or unground.

GUIDELINES FOR LEGISLATION ON DAPR

Because PRs vary widely in chemical and mineralogical composition, reactivity, particle-size distribution, and accessory minerals, it is important to recognize that any regulations concerning a PR for direct application should be related to its agronomic effectiveness. For example, a highly reactive, as-received, unground PR can be more agronomically effective than a finely ground, low-reactivity PR. If a regulation requires that PR be ground to less than 100 mesh (0.15 mm), then farmers may not be able to use more reactive, unground PRs that may provide more agronomic and economic benefits than the use of finely ground, low-reactive PRs for crop production.

The following guidelines are proposed for consideration by regulatory agencies involved in devising legislation on DAPR:

1. As the total P_2O_5 of a PR is not related to its agronomic effectiveness, a regulation that requires minimum total P_2O_5 content should be solely for the purpose of protecting users' from unscrupulous suppliers.
2. All of the current methods of solubility measurement for PR require only one extraction. As associated free carbonates and particle size can affect the solubility of apatite, it is recommended that the sequential two-extraction procedure be carried out in order to obtain a more actual solubility value of PR in the second extraction. For example, if a PR has a small fraction of very fine particle size, the solubility obtained in the first extraction can be relatively high because of the small particle-size effect. During the second extraction, the solubility measured represents the more actual solubility of the main bulk of PR particles after small particles are dissolved in the first extraction. The two-extraction procedure can also eliminate the depressive effect of free carbonates on apatite solubility of PRs containing a moderate content of free carbonate (e.g. less than 10 percent). Thus, it is recommended that a sequential two-extraction procedure be used with NAC and 2-percent CA. For 2-percent FA, this may not be necessary because of its relative strength that may eliminate the effects of free carbonates and small particle size on apatite solubility during the first extraction.
3. The PR solubility value can be elevated artificially if it is expressed as a percentage of total P_2O_5 . Therefore, when comparing PRs containing low total P_2O_5 content with PRs containing high P_2O_5 content, it is recommended that PR solubility be expressed as a percentage of rock. This eliminates the possible grade effect. This is particularly important when comparing solubility values of PRs that vary widely in terms of total P_2O_5 content.

4. For highly reactive PRs, the as-received, unground forms are almost as effective as the finely ground forms in agronomic use despite the fact that the solubility is lower with the unground forms. For low-to-medium-reactive PRs, both agronomic effectiveness and solubility are lower with the unground than the finely ground forms. Therefore, legislation should specify separate requirements for particle-size distribution for highly reactive and other less reactive PRs.
5. Although solubility affects the reactivity and potential agronomic use of the PR considerably, several other factors, such as soil pH and crop species, are also important in determining the ultimate agronomic effectiveness of the PR. For example, a highly reactive PR may not be effective for most of the food-grain crops grown on soils with a pH of more than six. A low-reactive PR may be agronomically effective for plantation crops grown on acid soils. Therefore, minimum solubility requirements should consider agronomic factors such as soil pH and crop species. One possible way of doing this is to establish a minimum solubility requirement of PR in different categories corresponding to different soil pH and crop species conditions.
6. The quality requirements for PR for chemical acidulation should not be the same as those for direct application. The factors that affect the acidulation process are not the same as those that are important for DAPR. For example, the sesquioxide ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) content of PR is critical for the production of H_3PO_4 and water-soluble P fertilizers whereas it is not a significant factor for DAPR. Therefore, legislation on quality control of DAPR should not be the same as that for acidulation.