A Sino-French Cooperative Project

Partially Acidulated Phosphate Rock

--- Background and Findings of the Research implemented---

(English edition)

Rukun LU, Liming XIONG, Zhengyuan SHI,
Truong Binh, Fayard C., Fok A.C.M. ,Pieri, C.

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部分酸化磷肥研究

——研究背景和研究结果——

鲁如坤 熊礼明 时正元
Truong Binh C. Fayard M. Fok , C Pieri

中国科学院南京土壤研究所（ISSAS）
法国农业研究发展国际合作中心（CIRAD）

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Foreword

In February 16 ~ 21, 1987, a meeting of the Sino-French Joint Committee on Science and Technology was held in Beijing and a project entitled "Agricultural Use of Chinese Medium- and Low-grade Phosphate Rock in China" or "Effective use of Chinese phosphate rock " was chosen as one of the collaborative projects between the two governments of China and France. It was also decided that the Institute of Soil Science, Academia Sinica (Chinese Academy of Sciences) (ISSAS) and the Centre de Cooperation Internationale en Recherche Agronomique pour le Developpement (CIRAD) were the joint implementing organisms of the project and that the actual contents of the project were "Research on Partially Acidulated Phosphate Rock (PAPR)". Scientists in charge of the project implementation was Prof. Rukun Lu, Assistant Director of ISSAS and Director of the Department of Soil and Plant Nutrition on the Chinese side and Dr. Christian Pieri, Deputy Director of CIRAD-IRAT (now CIRAD-CA), and Dr. Truong Binh, (Director of Laboratory, CIRAD-IRAT) on the French side. Major participants in the project were Dr. Liming Xiong and Senior Agronomist Zhengyuan Shi from the Chinese side and Research Engineer Michel Fok Ah Chuen (CIRAD-IRAT) and Mr. Christian Fayard, Technical Director of Timac S.A. Fertilizer Corp. on the French side. This book is a sum-up of the findings of the project.

In addition, the book also encompasses the findings of related researches accomplished by ISSAS in the 1970s (Chapter 8) and the results of the cooperation between

ISSAS and the International Rice Research Institute (Chapter 11). In order to help readers get an overall view, the book covers, as well, some thought-to-be important background information about research related to PAPR conducted in China and in the world.

Project Financing: ISSAS was the sponsor on the Chinese side, supported by the State Science and Technology Commission. CIRAD was the counterpart on the French side with support from the Ministry of Foreign Affairs and Ministry of Agriculture of the Republic of France.

ISSAS had involved a few more collaborators in the project, such as the Soil and Fertilizers Institute of Zhejiang Province Academy of Agricultural Science and some other local agricultural research institutions. Prof. Lu Rukun is the writer of the book. Prof. Dai Yuanfa, a well-known senior and prestigious specialist in P fertilizers in Shanghai Academy of Chemical Industry took charge of the Chapter Six and contributed to the introduction. We sincerely acknowledge his involvement as well as the support and help from associated institutions and experts to the project. Special thanks are addressed to Mrs Lin Le, former-Director of the P Fertilizer Department of the Ministry of Chemical Industry of China.

Introduction

Partially acidulated phosphate rock (PAPR) or partially solubilized phosphate (PSP) is also called acid-saving P fertilizer, which means that its production consumes less acid than it is necessary to fully decompose phosphate rock. This type of product contains some soluble phosphate, a limited amount of citrate soluble phosphate and non-decomposed phosphate rock powder. Acid consumption of PAPR generally accounts only for 20% ~ 80% of what is needed for superphosphate (normal superphosphate or double superphosphate). During the production process, sulfuric and phosphoric acid are generally used. When nitric acid or hydrochloric acid is used to acidulate phosphate rock, the resulting product contains highly soluble calcium nitrate or calcium chloride which are extremely susceptible to absorb moisture, thus affecting the product physical properties and causing difficulty in producing, marketing and applying the product.

0.1 General Status of PAPR Development

Since the 1960s, development of P fertilizers has been oriented toward high nutrient content and high solubility products, ammonium phosphate and double superphosphate are characteristic examples. But as far as the whole world is concerned the production of low-concentration type of fertilizers has not yet stop, because it is simple in technology and low in cost. Even direct application of phosphate rock powder still makes up 3% ~ 5% of the consumption of P fertilizers. This situation mainly depends on the conditions of a country or a region in producing P fertilizers, i.e. resources of the raw material (mainly phosphate and Sulfur mines), soil properties, conditions of agricultural production, transportation and integrated industrial capabilities, etc. (Hammond, 1990).

The major advantage of high-concentration fertilizers lies on cost saving in packing, storage, transportation, distribution and application. The cost incurred in marketing and distribution of low-concentration fertilizers often accounts for half the total expense the farmers pay for the fertilizers. High-concentration fertilizers have nutrients 2.5 ~ 4.5 times as much as low-concentration fertilizers do, and in terms of production cost per unit of product, the former is 20% ~ 30% higher than the latter. When the product has a long way to go and many hands to pass through before it reaches its destination and that the labor cost is high, the high-concentration type of fertilizers may be more economical. This is the main reason why the fertilizer industry has opted for high concentration fertilizer. In a country or a region where the fertilizer distribution network is geographically limited, few intermediary agents are involved and labor is not expensive, the low-concentration type of fertilizers may be more economical. In China, although the production of P fertilizers is oriented towards the high-concentration type, the low-concentration type still dominates in the current production.

Solubility of P fertilizers can be divided into three categories, water soluble, citrate soluble and unsoluble. Superphosphate, double superphosphate and ammonium phosphate are in Category One; fused calcium magnesium phosphate in Category Two; nitric phosphate partially in Category One and partially in Category Two; PAPR partially in Category One, partially in Category Two and partially in Category Three; and phosphate rock powder partially in Category Two and partially in Category Three. Criteria to choose among so many kinds of P fertilizers depend mainly on soil properties, annual precipitation, species of crops, etc. It is generally considered that soil properties determine the choice of P fertilizers of different water solubility (Jajji, 1985; Schultz, 1986; Hammond, 1998).

In China, in the regions south to the Yangtze River, there are large areas of acidic red soil, for which fused calcium magnesium phosphate has been promoted with significant efficient outcomes. During the 1950s ~ 1960s, efforts were devoted to developing direct application of phosphate rock powder, but little success has been achieved. The major cause is that China has not yet discovered so far any large reserves of soft phosphate ore. China is one of the countries that have most phosphate resources in the world, but these reserves are mostly of marine deposit, except a small portion which is of marine deposit transformed into metamorphic rocks。Most of the phosphate rock discovered in China is low in reactivity, much lower than that in Morocco. If application of phosphate rock powder is expected to have some reasonable response from the crop receiving it, soft phosphate ore high in reactivity should be selected for instance, Gafsa phosphate ore from Tunisia, North Carolina phosphate ore from the USA, Class C calcinated phosphate ore (aluminum phosphate) from Christmas Island, South Pacific, and guano from Peru and South Pacific islands.

However, when it comes to improve the nutrient status of newly reclaimed fields, phosphate rock powder low in reactivity is generally used.

China has large areas of acidic soil, but it lacks soft rock phosphate. As a result, the potential in extending the direct application of phosphate rock powder is limited. For this it is of great significance to conduct experiments on PAPR using domestic phosphate rocks. This is also the fundamental basis of the cooperation between ISSAS and CIRAD.

0.2 History and current situation of the PAPR development

In the 1930s, PAPR, first called Kotka Superphosphate, was a mixture of normal superphosphate and phosphate rock powder, because it was first produced industrially in Kotka, Finland. Compositions of superphosphate and Kotka superphosphate are listed in the table (Marwaba, 1992).

Table : P_2O_5 contents in superphosphate and Kotka superphosphate (% in weight)*

	Total P_2O_5	Available P_2O_5	Free acid P_2O_5	Free water
Superphosphate (Morocco)	21.4	20.2	1.7	9.8
Kotka superphosphate*	22.8	14.6	1.3	8.9

*: Mixture of superphosphate (Morocco) and phosphate rock powder (From Kola, Russia)

Today, the world has over a dozen of plants scattered in a number of countries producing PAPR. Many studies and experiments have been conducted on its effectiveness in relation to soil properties, there is a tremendous volume of literature and reports confirming unanimously that it is effective in acidic soils. PAPR not only attracts attention from developed countries, but it is also produced and utilized in some developing countries. In particular, developing countries in tropical and subtropical areas can produce this type of P fertilizers for their agriculture by making use of their own phosphate resources.

China started its research on PAPR in the 1960's, with the Sichuan Province Academy of Agricultural Science, ISSAS, and Shanghai Academy of Chemical Industry got committed one after another. All of them have achieved some useful results.

PAPR differs from superphosphate and double superphosphate only by a much less acid consumption in its production. It is not directed at a full or very high decomposition rate of phosphate rock. Actually, the decomposition rate obtained with PAPR is below 80% of the one achieved through direct and complete acidulation of phosphate rock. The decomposition rate of phosphate rock is positively related to its degree of acidulation. The so-called degree of acidulation refers to the value in percentage of acid consumption with that of superphosphate or double superphosphate set as 100%. Choice of degree acidulation depends mainly on characteristics of phosphate rock and soil properties. With phosphate rock higher in reactivity, its degree of acidulation can be set lower. On highly acidic soils, PAPR of low acidulation can be used, whereas on low acidic soils, it is better to use PAPR of high degree of acidulation. How to use PAPR economically should be based on reliable experiment results (Menon *et al.*, 1990).

Many acids can be used in the production of PAPR: sulfuric, phosphoric, nitric and hydrochloric acids. Sulfuric, phosphoric acids and mixture of the two are more commonly used. When nitric acid is used, PAPR contains phosphate and nitrate-N. But the calcium nitrate it contains is highly hygroscopic, affecting the characteristics of the product. It is reported that the product with acidulation less than 30% has good results in areas, which are not so humid. Addition of a small amount of sulfuric acid into the nitric acid may improve physical properties of the product. It is also reported that blending the product with some urea turns the calcium nitrate it contents into x $Ca(NO_3)_2 \cdot y\ NH_2CONH_2$, thus improving its physical properties and transforming it in the same into a NP compound fertilizer (Yadov, 1992).

Quite a number of countries and international research institutions are actively engaged in developing technologies and techniques for producing and utilizing PAPR. With support from FAO, the International Fertilizer Development Center (IFDC) has accomplished much work on the acidic soils and using local phosphate resources in the tropical and subtropical countries. It holds that PAPR has the following advantages: 1) It contains water soluble phosphate (readily available P) that can meet the crop's need at the early growing stage and stimulate healthy development of the rooting system, which enables to absorb more P from citrate soluble phosphate and unsoluble phosphate, thus ensuring P supply at the middle and late growing stages of the crop. 2) If phosphoric acid is used as acidulating agent, the product has a higher concentration of nutrients than superphosphate. 3) When sulfuric acid is used, the product can supply S to the soil which is very important in S-deficient soils. 4) PAPR production consumes much less acid than superphosphate or double superphosphate. If the degree of acidulation of the phosphate rock is 40% ~ 60%, the acid consumption per unit weight of the phosphate rock will be 40% ~ 60% lower, thus reducing its production cost. This makes special sense in countries or regions, which are short in sulfur resources or which have high production cost of sulfuric acid. 5) It can use phosphate rock of low grade as raw material. Of course, P_2O_5 grade, content of impurity, and reactivity of phosphate rock all have effect on quality of PAPR produced. 6) PAPR is also better than superphosphate or double superphosphate in physical properties, and particularly lower in free acid and free water contents. Besides, it does not pose any problem when mixed with urea.

China feels the need and has the conditions to extend the production and utilization of PAPR (Please refer to Chapter 5). The reasons are: 1) large areas of acidic soils concentrated mainly in the regions south to the Yangtze River, where the climate is warm with abundant rainfall; 2) rich phosphate resources low in production cost, relatively less sulfur resources and relatively higher cost in sulfuric acid production. Reducing sulfuric acid consumption will generate significant economic profit; 3) the existence of a large number of medium- and small-sized superphosphate plants, which can be easily modified into PAPR plants without much investment, if any; 4) adaptation to the market demand, since it can be applied directly into the field or used as raw material for blended fertilizers.

Readers can refer to a number of reviews that have been published in other countries on PAPR (Bolan, 1990; Gulolen, 1991; Gorboucher, 1981; Hammond, 1986; Stephen, 1986; Ragan, 1993).

Chapter 1. Generalities on the soil phosphorus status in China

About the soil phosphorus status in China, there have been some conclusive papers published (Lu Rukun, 1987; Xi Chengfan, 1998), displaying an overall insight. Nevertheless, China is a country of vast territory consisting in a huge diversity of soils. in addition, soil P is susceptible to various factors, natural and anthropogenic ones, consequently its status varies sharply. The fraction of available P, in particular, may change rapidly and vary significantly within a short distance and time. Therefore, it is essential to take into account the variation of soil P status in applying P fertilizers, in determining properly whole demand for P fertilizers in the country and in drawing plans for developing P fertilizer industry (Lu Rukun, 1990).

1.1 Soil total P

1.1.1. Total P content in the major types of soils in China

Total P content in the soils of China ranges roughly between 0.01% and 0.22%, but in most soils it is between 0.02% and 0.11%.

Table 1 – 1 shows that soil total P has a tendency to increase from south to north, which might be the result of the variation of weathering degree of the soils. Soils different in weathering are different not only in total P content, but also in ratio of different forms of P in total P (Lu Rukun *et al.* 1998). For example, Ca – P declines but O – P(occluded-phosphate) rises with the increase in weathering degree of the soils. In soils submitted to high temperatures, Fe – P dominates and furthermore Fe – P may be the major sources of P supply to rice.

Table 1-1 Soil total P in the major types of soils in China

Type of soils	Distribution	Parent material	Content (P%)
Latosol	Hainan	Granite, sandshale	0.013 ~ 0.026
	Leizhou Peninsula	Basalt	0.034 ~ 0.074
Red soil, Lateritic paddy soil	Hilly areas in Jiangxi,	Quaternary red clay, red sandstone	0.017 ~ 0.034
Yellow brown earth, bleached paddy soil	Ning-Zheng Hilly region in Jiangsu	Xiashu yellow earth	0.022 ~ 0.052
Brown earth	Shandong, Liaoning	Loessial deposit	0.043 ~ 0.086
Black soil, Albic black soil	Heilongjiang, Jilin	Loessial deposit	0.061 ~ 0.152
Yellow fluvio-aquic soil	North China Plain	Huang-Huai alluvium	0.043 ~ 0.096
Loessial soil	Loess Plateau	Loess	0.052 ~ 0.070
Aeolian desert soil	Xinjiang	Ancient alluvium	0.10 ~ 0.113

1.1.2. Effect of cultivation and fertilization on soil total P

Besides the climate differences, land shapes and human activities have much influence on soil total P content. In a hilly region, soil total P varies sharply from spot to spot within a short distance (Zang Huilin *et al.* 1965), this is believed to result from difference in land use pattern, cultivation and fertilization practices and status of erosion. In a plain region, variation of nutrient contents in soil can be observed through a pattern of concentric circles with a large village-town as their center.

Soil P varies not only with distance, but also significantly with time, even within a not very long time period. Listed in Table 1 – 2 are the results of a three-year experiment on a three-crops-a-year cultivation system (upland crop + 2 crops of rice) (Lu Rukun, 1998). After three years, available P dropped by 36.6 mg/kg in the control plots (0 – 0 – 0) where no P fertilizers were applied, but went up by 11 mg/kg in Treatment P – P – P, where P fertilizers were applied to all three crops. In Treatment P – 0 – 0 and Treatment P – P – 0, it did not vary so significantly. It is clear that soil P, both total P and available P, may show significant changes within a short period of time. Such a variation is closely related to soil P balance status (net input minus removal) ($r = 0.99$). Therefore, just in a short period of time, soils deficient in P may be turned into soils adequate in P while soils that show no crop response to P application turn to big response. The appearance of such phenomena in agricultural production is just the result of changes of soil P status.

Table 1-2 Balance and dynamics of soil P during land use (1976 ~ 1978)

Treatment	0 – 0 - 0	P – 0 – 0	P – P – 0	P – P – P
Total input (P_2O_5 kg/ha)	0	164	314	402
Total removal (P_2O_5 kg/ha)	-224	-259	-271	-276
Balance (kg/ha)	-224	-95	+43	+126
Changes in total P (P_2O_5 %)	-0.016	-0.004	+0.011	+0.014
Changes in available P (P_2O_5 mg P/kg)	-36.5	-20	+6	+11

1.1.3. Soil total P and P supply

It was discovered long ago that soil total P could not be used as an accurate indicator of soil P supplying power. This is because a large proportion of soil P is in a slowly available form and, moreover, the content of available P is not always related to the content of total P in the soil. However, it is also noticed that although high soil total P does not necessarily mean adequate soil P supply, low soil total P may indicate inadequate soil P supply. In a number of provinces or regions, when soil total P is found below a certain level, inadequacy of soil P supply will appear. For instance, data from Zhejiang Province show that when soil total P fell below 0.04%, yields of green manure crops, rapeseed and wheat responded significantly to P fertilization. Data from Jiangxi Province revealed that when soil total P was lower than 0.04%, P fertilizers raised the yield of every crop, rice yield increased by 30% or so, when soil total P ranged between 0.02% and 0.03%, and by 15% ~ 30% when soil total P was between 0.03% and 0.04%. Results from research works in Sichuan, Guangxi and Guangdong Provinces demonstrated that when soil total P ranged from 0.02% to 0.045%, crop response to P fertilizers could be found on every crop. It is quite obvious that the relationship between soil total P and effectiveness of P fertilizers involves a series of factors. Statistical analysis from 164 field experiments showed that in most cases when soil total P was below 0.04%, it was more likely to see crop response to P fertilizers (Lu Rukun *et al.* 1987).

1.2 Available P levels in soils of China

Available P (Olsen method) level in soil is a direct indicator that determines soil P supply capacity and it is also the most fundamental basis for recommendation of P fertilization.

Soil available P is the most sensitive indicator among the soil available nutrients and it is highly affected by cultivation and fertilization. Long-term experiments show that soil available P varies greatly and quite regularly during cultivation, this is mainly because soil P suffers no substantial losses.

1.2.1. Soils rich in available P in China

The so-called soils rich in available P refer here to those with soil available P above 20 mg/kg. At this level, crops can generally have adequate P supply from the soil without P fertilization. Of course, in cold regions or with regard to high-P-demanding crops (potato, etc.), P fertilization remains essential. The proposed value is however suitable to be used as the indicator of P abundance in soil.

It can be observed from Table 1 – 3 that the acreage of cultivated land with soil available P higher than 20mg/kg is not large in China. With province or region as a unit, there is not any province with more than 75% of its total cultivated acreage being rich in available-P.. Only Xizang Autonomous Region (Tibet) has more than 50% of its cultivated land with soil rich in available P. Most provinces or regions only have less than 10%.

Table 1-3 Percentage of cultivated land with soil available P (Olsen method) over 20 mg/kg

Percentage (%)	Class	Province or region *
> 75	I	-
50 ~ 75	II	Xizang
25 ~ 50	III	Fujian, Heilongjiang
10 ~ 25	IV	Yunnan
<10	V	Beijing, Tianjin, Jilin, Inner Mongolia, Hebei, Henan, Shanxi, Shandong, Anhui, Jiangsu, Zhejiang, Jiangxi, Hunan, Hubei, Guangdong, Guangxi, Hainan, Shaanxi, Gansu, Qinghai, Xinjiang, Guizhou, Sichuan.

*: Information about some individual provinces or regions not included in the table.

In terms of the actual acreage of this rich P type of soils, although Xizang is high in percentage, its actual acreage is very small. Yunnan is the only province that has an acreage over 660 000 ha , and Heilongjiang the only one over 3 300 000 ha. It is clearly shown that soils rich in available P account only for a limited percentage of the total cultivated land in China.

1.2.2. Estimation of the acreage of cultivated land deficient in P in China

In China soils deficient in P, amounting to about 67 millions ha (Tang Jinchun, 1996), are mainly calcareous soils in the northern part of China, Albic black soil in Northeast China, red soil, purplish soil and low-yield paddy soils, etc.. The so-called P deficient soils here are those defined with soil available P less than 10 mg/kg. Of course, this is only a rough frontier line. Table 1 – 4 shows the percentage of cultivated land with soil available P below 10 mg/kg in the provinces and regions of China.

Table 1-4 Percentage of cultivated land with soil available P below 10 mg/kg in the provinces and regions of China

Percentage (%)	Class	Province or region *
> 75	I	Tianjin, Jilin, Inner Mongolia, Hebei, Henan, Shanxi, Shandong, Anhui, Jiangsu, Zhejiang, Jiangxi, Hubei, Guangxi, Hainan, Shaanxi, Gansu, Xinjiang, Sichuan.
50 ~ 75	II	Beijing, Hunan, Guangdong, Qinghai, Yunnan, Guizhou,
25 ~ 50	III	Fujian, Heilongjiang, Xizang,
<25	IV	–

*: Information about some individual provinces or regions not included in the table.

It is clearly shown in Table 1 – 4 that provinces or regions with a share of cultivated land deficient in P which is over 75% are scattered all over the country. This is the fundamental cause that explains why the production of P fertilizers is the second largest fertilizer industry.

In order to provide readers with an idea of absolute values of the acreage of the land being involved beyond the one of relative value, the province and regions are sorted into grades in terms of acreage of land deficient in P in Table 1 – 5.

The critical value of 10 mg P/kg (Olsen method) is used to sort P-deficient soils only in the case of dealing with crops in general. It is lower for some P sensitive crops, but higher for rice. As rice is the grain crop that has the largest cultivation area in China (301.71 million mu, Chinese Agricultural Yearbook, 1995), it is essential to take into account this characteristic of rice in identifying P-deficient soils in China. This is particularly important to the provinces in South China where rice is the major staple food crop.

Table 1-5 Grading of provinces and regions in terms of acreage of cultivated land with soil available P below 10 mg/kg

Grade (million ha)	Province or region*
> 6.00	Inner Mongolia, Hebei, Henan, Anhui, Shandong, Sichuan
4.67 ~ 6.00	Jiangsu
3.33 ~ 4.67	Heilongjiang, Jilin, Shanxi, Hubei, Shaanxi, Gansu, Xinjiang
2.00 ~ 3.33	Jiangxi, Hunan, Guangdong, Guangxi, Yunnan, Guizhou
0.67 ~ 2.00	Fujian, Hainan
< 0.67	Beijing, Tianjin, Qinghai, Xizang

*: Information about Shanghai, Zhejiang, Ningxia, Liaoning and Taiwan not included in the Table.

1.3 Serious P-deficient soils in China

Crop response to P fertilizers increases with the extent of P deficiency in the soil. Therefore, crop response in soils seriously deficient in P will be greater than in soils slightly deficient in P when the same amount of P fertilizers is applied. In the following paragraphs, soils seriously deficient in P in the provinces will be addressed briefly.

The critical value for soils seriously deficient in P is set at 5mg/kg · P (Olsen method). Soils at this level call for P fertilization for every crop. The above-mentioned acreage of soils with soil available P below 10mg/kg

(Olsen method) includes this portion of soils seriously deficient in P, to which a special attention will be devoted here.

In Table 1 – 6 and Table 1 – 7 are classifications of provinces according to the shares and the acreage of soils seriously deficient in P. It is clearly shown that soils seriously deficient in P are also concentrated in the North China Plain, Inner Mongolia, Northwest China and Sichuan Province.

Table 1-6 Distribution of soils seriously deficient in P in China (% of the total area of cultivated land)

Percentage	Provinces or regions*
> 75	-----
50 ~ 75	Tianjin, Inner Mongolia, Hebei, Henan, Shanxi, Shandong, Jiangsu, Hubei, Guangxi, Hainan, Xinjiang, Sichuan,
25 ~ 50	Jilin, Anhui, Zhejiang, Jiangxi, Hunan, Guangdong, Shaanxi, Gansu, Yunnan, Guizhou
< 25	Beijing, Heilongjiang, Qinghai, Xizang

*: Information about some individual provinces or regions not included in the table.

Table 1-7 Classification of provinces according to acreage of soils seriously deficient in P in China

Grade (million ha)	Provinces or regions*
> 6.00	Sichuan
4.67 ~ 6.00	Inner Mongolia, Henan, Shandong, Anhui
3.33 ~ 4.67	Hebei, Jiangsu
2.00 ~ 3.33	Jilin, Shanxi, Shaanxi, Gansu, Xinjiang
0.67 ~ 2.00	Heilongjiang, Jiangxi, Hunan, Guangdong, Guangxi, Hainan, Yunnan, Guizhou
< 0.67	Beijing, Tianjin, Fujian, Qinghai, Xizang

*: Information about some individual provinces or regions not included in the table.

Chapter 2. Phosphate rock resources in China and in the world

It is estimated that out of the total P reserve of the globe, a major portion, around 96 ~ 160 billion tons, exists in the soils of the earth, while about 80 billion tons are dissolved in the seawater. P in the ore form is estimated to be around 19 billion tons (P).

Phosphate mines are not renewable resources and most of them belong to the type of $Ca_{10}\ (PO_4,CO_3)_6(F,OH)_2$. Only a limited number of mines are sediments of aluminum phosphate, like svanbergite in Sichuan, China.

Most Phosphate ores contain impurity of varied quantity, for instance, silicon, ferric oxide, aluminum, calcium, magnesium (limestone or dolomite), etc. which cause difficulties while processing.

The pattern of mining of phosphate deposits depends on the nature of sediment. Generally, open pit mining is adopted for mines that have not yet been solidified, or are buried shallow and in bed, while for mines that have been solidified and are buried deep, shafts have to be built in mining.

Phosphate ores often have to be beneficiated due to having a low content P content. Whether the process is easy or not depends on properties of the ore. For instance, fluorapatite carbonate is easier to handle than fluorapatite. Of course, properties of the impurity also have a great impact on the process.

It is very likely that as soon as agriculture appeared on the earth, man began to make use of P containing material as for instance manure, night soil, barnyard manure, bone, etc. Nevertheless, it was not before 1840 that Liebig J. Von., a German, suggested using acid to dissolve bone powder as fertilizer, unfolding then the history of the production of P fertilizers, but Escher, an Austrian, was the first use acid on phospate rocks. About 85% of the ores extracted from phosphate mines are used for P-fertilizer production.

2.1 Phosphorus Resources in China

2.1.1. Characteristics of the phosphate resources in China

The phosphate resources of China are mainly distributed in Yunnan, Guizhou, Hubei, Sichuan and Hunan Provinces, forming 8 major ore fields, 1) Dianchi Ore field. The field, consisting of seven branch ore fields, i.e. Kunyang, Haikou, Jinning, Jianshan, Jiangchuan, Chengjiang and Anning, strides over Kunming City and Yuxi Prefecture of Yunnan, and covers a land area of 1200 km^2; 2) Kaiyang Ore field. Located in Kaiyang of Guizhou, the ore field consists of seven allotments, i.e. Maluping, Yongshaba, etc. covering an area of 55 km^2; 3) Wongfu Ore field. It has nine allotments, spreading out in Wengan and Fuquan Counties in central Guizhou and covering an area of 58 km^2; 4)Yichang Ore field. It stretches over a land area of 300 km^2 in Yichang, Yuanan and Xingshan counties of Hubei and has a total of 10 branch ore fields; 5) Huji Ore field. It covers a land area of 115 km^2 striding over Zhongxiang and Yicheng counties of Hubei and consisting of 27 allotments, i.e. Wangjie, Dayukou, Niuxinzhai, etc.; 6) Baokang Ore field. Located within Baokang County of Hubei, it spreads out over an area of 800 km^2, consisting of 6 allotments, i.e. Baizhu, Maqiao, etc.; 7) Jinhe-Qingping Ore field. It is in Shifang and Mianzhu counties in central Sichuan and made up of two ore fields, i.e. Jinhe and Qingping; and 8) Mabian Ore field. Consisting of four branch ore fields, it covers an area of 45 km² in Mabian County in south Sichuan. During the late 1990s, China conducted a systematic study on phosphate resources of the country, addressing comprehensively their basic characteristics as follows (Jiang Shanxiang, 1999):

- ***China has large reserves, but under the current conditions the exploitability of the reserves is quite low.***

By the end of 1990, the reserve of phosphate in China had been estimated to be 10,848 million tons with an average P_2O_5 content of 20.36%; ranking China among other countries, like Morocco, USA and the former Soviet Union, known to have abundant phosphate resources. Among the reserves of China, about 51.62% can be defined as industrial ores (Grade A + Grade B + Grade C). Based on the reserve evaluation model established in the study and the results of the evaluation of over 308 mines, it is shown that only 82 have an exploitation rate over 60%. It is preliminarily estimated that under the current economic and technological conditions, only around 10% of the total reserves is exploitable, equaling to about 800 million tons in terms of standard phosphate ores.

- ***The reserves are distributed mainly in five provinces, Yunnan, Guizhou, Hubei, Sichuan and Hunan.***

The phosphate resources of China are concentrated in the Yangtze paraplatform, which is made up of Sichuan-Yunnan metallogenetic band, Guizhou-Hubei metallogenetic band and West Hunan metallogenetic band. The reserves in Yunnan, Guizhou, Hubei, Sichuan and Hunan amount to 95.20% of the country's total and are relatively higher in content than those in other provinces. Concentration of the reserves facilitates large-scale exploitation, but its disadvantage is that the phosphate rock and phosphate fertilizers have to go a long way to their destination for processing or consumption.

- ***The phosphate beds are dominated with phosphorite rock.***

Phosphate beds can be divided into three types, all of which are encountered in China. The type of sedimentary phosphate accounts for 95.79% of the country's total reserve. As it was formed mainly during the Sinian and Cambrian and the Devonian as well, much earlier than the reserves in Morocco and Florida of USA were (from Late Cretaceous to Miocene) and the rocks are much harder.

- ***Most of the beds are slightly-slant to slant and moderate in thickness.***

Amounting to around 70% of the country's total reserve, this type of orebody is usually $15^{o} \sim 45^{o}$ in obliquity, ranges between 5 m and 15 m in thickness, and does not vary much in thickness, P content and obliquity within an ore field. But the exploitation of this type of orebody comes along with a series of problems, such as low exploitation rate, great loss ratio resulting poor P content level, difficulty in acquiring adequate equipment and insecurity in production. In most of the ore fields, however, the phosphate rocks and the host rocks are stable or fairly stable, which is a favorable condition for underground exploitation to adopt the null field method; and the hardness and specific weight of the phosphate rocks are moderate, which makes them adaptable to most forms of transportation, such as pipeline, rubber band conveyer, plate type conveyer, etc..

- ***Direct apical and antapical plates and interlayers are mostly of dolomite.***

The direct apical and antapical plates and interlayers of majority of the phosphate mines in China are of dolomite (silicate containing dolomite, dolomitized limestone). During exploitation, the intermingling of host rocks increases MgO content in the output from the mine, thus affecting processing behavior of the phosphate rocks.

- ***Most of the phosphate rocks are middle and low in P content but high in impurity.***

The average P content of the phosphate rocks in China is 20.36%, falling into the category of middle and low grade in content. According to the statistics of the "Systematic Study of Exploitation of Phosphate Resources in the Country", among the 308 mines, there are only 7% with P content over 30%, of which a considerable proportion, however, is difficult to exploit separately; 15% with content ranging between 25% and 30%, 25% with content of 25% and 53% with content lower than 20%.

Within the phosphate impurities, the MgO content is generally over 1.5% and mostly over 3%; and the content of R_2O_3 is around 3% and could be over 5% in few cases. Hence, it can be concluded that China does not have much rich phosphate ore.

- ***Dressability of most phosphate rocks is poor.***

Of the phosphate rocks in China, the usable minerals are mainly micro-fine crystalline low-C fluorapatite, minimum-C fluorapatite (generally termed nauruite). The minerals are often in aggregation (impure) and some in fibre, which are difficult to be separated from gangue minerals. The gangue also contains high carbonate minerals, very close to nauruite in physico-chemical properties. In banding ores, does exist quite a large number of phosphate bands, but which are thin and impure. Therefore, more than half of the phosphate rocks in China is hard to dress.

- ***Geological conditions of some of the mines are rather complex.***

An overwhelming majority of the phosphate mines are located amid mountains, which are high and abrupt in landform, with high rainfalls in the southern part of China. Exploitation of the mines have disturbed the relatively stable massifs, which makes them sensitive to avalanches, landslides and has induced mud rock flows after heavy rainfalls. As carbonate rocks are widely distributed in the ore fields, karst develops, making the geological conditions even worse. Consequently, it is essential to study carefully the environmental geological conditions of a mine in specifying the anti-seepage and deploitation systems of its gangue bank, arranging its industrial sites and making choice of patterns and routes of its transportation.

- ***Transportation conditions in a large number of ore fields are quite poor.***

Most of the phosphate ore fields in China are located amid high and abrupt mountains with poor transportation conditions. For instance, Mabian, Yichang, and Baokang ore fields are over 100 km away from railway trunks. If the construction of a mine is to be considered,, the investment in building railways to connect it with a railway trunk would equal the investment of the mine itself.

- ***Environment concern limiting the development scale of most ore fields***

In exploiting phosphate resources, it is essential to pay attention to protection of the environment. This is a requisite set in the policy of China. Some ore fields lie just next to a nature reserve. For instance, the Mabian ore field adjoins the Dafengding National Second Class Nature Reserve, which is a habitat for panda, an animal under the state first class protection and a habitat for some other rare and precious animals and plants; within the Baokang ore field, there is a national fourth class nature reserve for wild *calyx canthus*; and within the Yichang ore field, though quite a distance away from the Shennongjia National First Class Nature Reserve, there is a fair number of state-level rare and precious animals and plants living in it.

The phosphate ore fields of China are mostly located at the upper-reach regions, where the surface water systems are generally tributaries of the second class or over. Low in water flow and water environment capacity, they are high-demanding in water pollution control, and to be protected mostly according to the standards for the third category of waters (sources of drinking water) in the surface water environment. For instance, the phosphate mines in Dianchi region are mainly distributed around the Dianchi Lake, including the Wuxian Lake and the Xingyun Lake. The Dianchi Lake is the major source supplying water to the industry, agriculture and urban daily life of Kunming City. So any potential pollution of the waterbody must be controlled.

Maybe, it can be considered that the phosphate resources of China are characterized by the dominance of ancient phosphate rock, which is a hard-to-dress type of ore, whereas the easy-to-exploit and easy-to-dress type of resources of loose and soft rock phosphate and coarse-crystallized apatite is relatively in shortage in

China.

2.1.2. Types of phosphate rocks in China and their chemical properties (Jiang Shanxiang, 1999)

On the earth over 200 kinds of minerals that contain over 1% P_2O_5 have been detected, but only those of the apatite family and the aluminum phosphate family are high enough in P_2O_5 content to be used for industrial purpose. The former is the dominant type. Bucenske, a Russian scientist, divides the family into fluorapatite, hydroxyapatite, carbonate apatite, francolite and karskite, with the first one dominating the family in reserve. Pure fluorapatite, however, rarely exists in nature. The chemical structure of apatite is often found to have atom replacement (isomorphous replacement), with CO_3^{2-} or F- taking the place of PO_4^{3-}, thus forming carbonate fluorapatite of varying degree. Having studied some major phosphate beds, the Geology Institute, Chinese Academy of Sciences, sorts phosphate rock into fluorapatite, minimum-C fluorapatite, carbonate fluorapatite, low-C fluorapatite, and high-C fluorapatite (Table 2 – 1). Minerals of aluminum phosphate are also exploited in some countries, for instance, the Palo phosphate mine in Senegal. The svanbergite mine in the Jinhe Ore field in China also belongs to this family and is being exploited. In the family, there are also bialite, calciowavellite and millisite, which can often be found in weathered and leached ores.

Before 1949, although China had already discovered phosphate mines in Jinping, Kunyang, Fengtai and Xisha Island, no further work was done. After 1949, besides prospecting in those places (except Xisha Island), China has discovered and prospected one after another dozens of large-sized phosphate mines and hundreds of moderate- or small-sized in phosphate beds in Guizhou, Hubei, Hunan, Yunnan, and Sichuan. Large volumes of geological studies indicate that China has almost every type of phosphate mines, e.g. endogenetic, sedimentary, metamorphic, guano cumulative deposits, and secondary leaching phosphate mines. Sedimentary type is in dominancy, metamorphic and endogenetic types are limited in number while secondary and guano cumulative types are so small in size and reserve that they are of no big nation-wide significance.

a Endogenetic phosphate deposit

Most endogenetic deposits are of magmatic apatite and some of hydrothermal apatite and pegmatitic apatite.

Apatite minerals have crystallized directly out of melted magma and got enriched into magmatic apatite deposits. On the earth, large-sized magmatic apatite deposits are mainly distributed in the former Soviet Union, South Africa and Brazil. Those famous apatite deposits are all associated with alkaline rocks, while the magmatic apatite deposits in China are related to intrusion of basite and superbasite. And they are mostly moderate- or small-sized ones distributed mainly in North China, Northeast China and Shandong Province. Although quite low in P content, they often have magnetite, vandadium titanium and so on in association, and they are suitable for multiple utilization.

The Fangshan phosphate mine in Hebei is a large-size apatite deposit of endogenetic type being discovered in China. The orebody formed amid pyroxenite in three strata over 2000 m long and $25^o \sim 40^o$ in obliquity. The mean thickness of a single stratum is 3 m, with the thickest being 14 m. The ore appears in blocky and impregnation structure, granular structure and spongy aerosiderite structure. Phosphate minerals are fluorapatite, hydroxyapatite and magnetite. Gangue minerals are mainly octobolite, biotite, potash and feldspar. The ore is rather coarse in granularity (0.2 mm) and easy to dissociate and dress. The ore contains 11% ~ 15% of P_2O_5 and 12% ~ 13% of Fe. Magnetite is suitable for multiple utilization.

b Sedimentary phosphate deposit

In 1937, Kachakoff suggested the theory of chemical genesis of phosphate rock that biological remains emit CO_2 when decomposed at the bottom of an ocean. The deeper is the deposit, the higher the content of CO_2 in the seawater, the greater is the pressure and the more phosphate is dissolved in the seawater. However in places (beyond 1000 m in depth) that are too deep for biological remains to reach, the content of P_2O_5 is lower. When seawater at the depth of the ocean flows to shallow seas along the coast, water temperature rises and pressure declines. As a result, from the water, a large volume of CO_2 escapes and P_2O_5 precipitates due to decreased solubility and gradually forms into phosphate rock deposits. In the 1960s, some scientists supplemented with the mechanism of deep seawater movement (upward movement of ocean current), stating that the existence of high barometric pressure in the mid-latitude region of the earth induces movements of winds. The water in the ocean moves with the winds forming ocean surface currents, which causes upward movement of deep seawater for supplementation, thus forming upward ocean currents.

Distributed mainly in the Yangtze paraplatform, the phosphate rock deposits in China were formed primarily during the Sinian, Cambrian and Devonian as well. The deposit at Tianzhu of Gansu is an exception, formed during the Ordovician period. In South China, sedimentation of phosphate nodules was found in the Permian Gufeng Horizon, but their P_2O_5 content was too low to be exploited economically.

- ***Sinian phosphate rocks***

The Doushantuo Group of the Upper Sinian Rang is the major horizon where phosphate rocks may exist in South China. It is widely spread in Guizhou, Hubei and Hunan provinces. Kaiyang, Wongfu, Yichang, Baokang, Huji and Shimen phosphate ore fields have ultra-large-size with a reserve over 100 million tons each. The Zhaoyang Phosphate Mine in Shangrao of Jiangxi is also a large one of that period with a reserve from 50 to 100 million tons. Besides, there are a number of moderate- (5 ~ 10 million tons) and small- (1 ~ 5 million tons) size deposits in Yunnan, Henan and Shaanxi.

In the above-mentioned large-size ore fields with a reserve of several to a dozen hundred million tons each, there are usually one and two ore horizons or three individually. The horizons are generally 3 ~ 8 m thick each and individually 15 ~ 20 m, extending over a dozen to several dozen kilometers. Based on their geological structures, landforms or requirements of exploitation, an ore field may be divided into several or a dozen allotments. Each allotment stretches over 2 ~ 5 km. Their orebodies are usually $15^{o} \sim 30^{o}$ in obliquity, with some below 10° and some individuals ranging between 70° and 80°. Their apical and antapical plates and interlayers are mostly of P containing dolomite and for some individuals of shale or silicalite.

Their P-containing minerals are mainly of low-C fluorapatite, and minimum-C fluorapatite, with gangue minerals being dolomite, calcite, chalcedon, feldspar, clay and kaolinite. The ore is often in the form of sand cutting, gel, pseudo-oolite， gravel debris, granule or fibre, etc. and structured mainly in the shape of block or stripe, and some in the shape of lump, laminated striation, rubble or worm.

Their P_2O_5 content varies from 34% ~ 36%, the highest (the ores in the allotments at Yongshaba of Kaiyang, Maluping, etc. are the best among the ancient rock phosphate on the earth), to 15%, the lowest (in Wangji allotment ph_3 horizon), with the majority being 21% ~ 25%. Their MgO content is generally 2% ~ 4.5%, with some individuals reaching up to 8% ~ 9%. Their ores are basically of silicocalcium in character, except for high-grade ores in some mines that are of silica in character. Some individual deposits are high in iodine content. For instance, in the Yingping Allotment of the Wengfu Ore field, it reaches 76 $mg.kg^{-1}$. Table 2 – 2 shows the main chemical composition of the ore in the typical allotment of each ore field.

Table 2-1 Classification of P-containing minerals in phosphorite deposits

Mineral		Fluorapatite	Minimum-C fluorapatite	Carbonate fluorapatite	Low-C fluorapatite,	high-C fluorapatite
Chemical formula		$Ca_{10}P_6F_2$ ∫ $Ca_{10}O_{5.9}C_{0.1}O_{23.9}(F,OH)_{2.1}$	$Ca_{10}O_{5.9}C_{0.1}O_{23.9}(F,OH)_{2.1}$ ∫ $Ca_{10}P_{5.75}C_{0.25}O_{23.75}(F,OH)_{2.25}$	$Ca_{10}P_{5.75}C_{0.25}O_{23.75}(F,OH)_{2.25}$ ∫ $Ca_{10}P_{5.5}C_{0.5}O_{23.5}(F,OH)_{2.5}$	$Ca_{10}P_{5.5}C_{0.5}O_{23.5}(F,OH)_{2.5}$ ∫ $Ca_{10}P_{5.0}C_{1.0}O_{23}(F,OH)_{3.0}$	$Ca_{10}P_{5.0}C_{1.0}O_{23}(F,OH)_{3.0}$ ∫ $Ca_{10}P_{5-x}C_{1+x}O_{23-x}(F,OH)_{3+x}$
Chem. composi-tion (%)	CaO	56.08	56.08	56.08	56.08	56.08
	P_2O_5	42.58 ~ 41.87	41.87 ~ 40.81	40.81 ~ 39.04	39.04 ~ 35.49	<35.49
	CO_2	0.00 ~ 0.44	0.44 ~ 1.10	1.10 ~ 2.20	2.20 ~ 4.40	>4.40
	F	3.80 ~ 3.61	3.80 ~ 3.42	3.80 ~ 3.42	3.80 ~ 4.18	>3.80
	H_2O	0.00 ~ 0.18	0.09 ~ 0.45	0.27 ~ 0.63	0.45 ~ 0.90	>0.72
Refringence(mean)		>1.628	1.620 ~ 1.628	1.615 ~ 1.620	1.608 ~ 1.615	<1.608
Birefringence		0.005	0.000 ~ 0.002	Null or extremely light	Null	Null
Density g/cm^3		3.200 ~ 3.170	3.175 ~ 3.130	3.150 ~ 3.135	3.135 ~ 3.112	<3.112
Space unit parameter	A_0	9.36 ~ 9.38	9.345 ~ 9.360	9.33 ~ 9.345	9.310 ~ 9.330	<9.310
	C_0	6.88	6.88	6.88	6.88	6.88
Crystal habit		Granular euhedral crystals or columnar giant crystals	Anhedral fine crystalline grains and cryptocrystalline or colloid	cryptocrystalline or C	colloid	Colloid
Citrate soluble P_2O_5(%)		Extremely low ~ low	Low ~ moderate	Moderate ~ high	High ~ extremely high	Ultra-high
Geological attitude		Moderate-sized mines of sedimentary metamorphic phosphate ore horizons (apatite). Endogenetic small-sized (giant crystal rocks)	Slightly transubstantiated sedimentary phosphate rocks (large-sized deposits); terrestrial supergenetic deposits (very limited). Sill-like or nodule-like deposits of marine sedimentary phosphate rocks of slightly acidic media (moderate- or small-sized), often coexisting with large volumes of organic matter	Marine sedimentary phosphate rocks with near-neutral media (large-sized sill-like deposits), often among black shale and carbonatite strata.	Marine sedimentary phosphate rocks with slightly alkaline media (moderate- or small-sized deposits) often coexisting with carbonate minerals.	Phosphorus nodules formed during lithogenesis (moderate- or small-sized deposits)

Table 2-2 Main contents of chemical elements in typical Sinian phosphate rock (%)

Element	Yong shaba Kaiyang	Yingping Wongfu	Zhangshu ping Yinchang	Baizhu Baokang	Hujie	Wang jie	Feng Xiang po
P_2O_5	36.78	29.08	25.64	22.49	22.88	15.26	15.54
CaO	51.04	47.13	38.38	36.80	38.51	30.72	34.57
MgO	0.62	5.12	2.93	4.38	2.26	6.15	9.04
CO_2	1.88	10.02	6.57	10.10	8.48	14.89	21.35
Fe_2O_3	1.32	0.42	1.62	1.38	2.33	1.52	0.78
Al_2O_3	1.23	0.61	1.48	0.88	3.55	1.06	0.76
SiO_2	1.91	3.78	15.29	16.95	16.60	27.49	15.19
F	3.64	2.92	—	2.06	1.91	1.63	1.24

- ***Cambrian phosphate rocks***

More widely distributed than Sinian ones, Cambrian phosphate rocks are divided into two types, the northern one and southern one with the Qinling Ancient Land and the Huaiyang Ancient Land as boundary.

A. Southern type:

The Meishucun Group of the Lower Cambrian Rang is another important horizon in the southern part of China. Its phosphate rock deposits are still distributed in the Yangtze Paraplatform mainly alongside the Kangdian Ancient Land, from eastern Yunnan to southern Sichuan. When extending east to Guizhou, the orebody gets thinner. For instance, in the Niutidang Group of Guizhou and Hunan, extensive distribution of phosphate rock deposits can be found with some useful elements in company, such as Mo, V, U, etc., but their orebody is only 0.4 ~ 0.8 m thick, too thin to be exploited.

Along the band from eastern Yunnan to southern Sichuan, there are several important large-size phosphate ore fields, such as Kunyang, Jianshan, Haikou, Anning, Jinning, Chengjiang, Mabian, and Hanyuan. Generally they have two horizons each and some individuals only one. The horizons are generally 3 ~ 8 m thick each and individually 31m, extending over several to a dozen kilometers. The horizons are usually 15° ~ 35° in obliquity, with some below 10° and some individuals ranging between 70° and 80°. Their apical and antapical plates and interlayers are mostly of dolomite and for some individuals of shale or silicalite.

Their P-containing minerals are mainly of low-minimum-C fluorapatite, with gangue minerals being mainly dolomite, quartz, calcite, and kaolinite and secondarily chalcedon, feldspar, mica and glauconite. The ore is often in the form of fine debris, sand cutting, pseudo-oolite， spherolite, etc. and structured mainly in the shape of compact block or stripe, and some in the shape of laminated striation or nodule. Their average P_2O_5 content varies from 21% to 25% and mean MgO content from 3% to 6%. Their ores are basically of silicocalcium in character and some of silica. For instance, the deposit at Deze contains 0.4% of MgO and 37% of SiO_2

In Dianchi, due to the unique phosphate rock deposit forming conditions and physical geographic conditions there, weathered phosphate rocks are extensively developed. With the landform in the ore fields rather smooth, ore bodies pop out on the slope or lie under a thin superficial layer. Low groundwater table facilitates percolation of water through the orebody. Under the action of slightly acidic groundwater, carbonate minerals in the ore are decomposed, forming $Ca(HCO_3)_2$, $Mg(HCO_3)_2$ solution running away with groundwater. The leaching of carbonate minerals help raise P content of the ore, and at the same time make silicate minerals argillized and easy to get dissociated. So in dressing the ore, it is easy to wipe the slob off the filter. Low Mg-containing headings are thus acquired.

Besides in Dianchi, weathered phosphate rocks are also found in Mabian and Hefeng (Sinian deposit) phosphate mines. In fact, weathering of phosphate is quite common, even on endogenetic and metamorphic phosphate. In Dianchi, the weathering is so strong that MgO content in the chemical composition of the ore rocks listed in Table 2 – 3 is universally lower than in the Sinian phosphate rocks.

Table 2-3 Main contents of chemical elements in the southern type Cambrian phosphate rock (%)

	Kunyang	Jinning	Jianshan	Haikou	Anning	Mabian	Hanyuan
P_2O_5	28.16	26.24	26.61	24.87	22.68	24.37	23.69
CaO	39.08	35.97	38.42	38.17	37.41	42.44	31.97
MgO	1.31	0.69	2.26	1.55	4.43	5.49	1.25
CO_2	4.83	3.29	6.27	6.13	9.25	13.00	4.83
Fe_2O_3	1.59	1.61	1.06	—	1.24	1.37	3.25
Al_2O_3	2.22	1.68	1.34	3.62*	1.66	1.42	5.17
SiO_2	15.02	25.34	20.92	22.27	17.86	7.72	22.98
F	2.65	2.34	2.48	2.50	2.13	2.46	**3.61

Note: * for K_2O and ** for R_2O_3 3.62%

B. Northern type

The depository phosphate rocks in Fengtai of Anhui, Xinji of South Henan, Tiantaishan and Yangpingguan of Shaanxi, and Suyukou of Ningxia were formed during the Suyukou Period and the Xinji Period, a bit later than the Meishucun Period in the south. Except the Tiantaishan deposit, which is a large-size one, all the mines in the north are moderate- or small-size ones. Their orebodies appear in stratiform, quasi-stratiform or podiform, relatively thin in thickness, 1 – 4 m, stretching over several to a dozen hundred meters and tilting at 15^o – 30^o. Their P-containing minerals are mainly of francolite, with gangue minerals being mainly quartz, dolomite, and sericite, and secondarily chalcedon, calcite, and other silicate minerals. The ore is often in the form of sand cutting or fine debris, and structured mainly in the shape of sheet, band, block or rubble. Their average P_2O_5 content is a bit lower than the southern type's, being 13% to 16% in general and average MgO content lower, too, from 2% to 3%. Their ores are basically of silicocalcium in character and some individuals of kiesel. The Tiantaishan deposit also has Magnesium carbonate in association, both exploitable.

- ***Devonian phosphate rocks***

Of the Shawozi Group of the Mid-Devonian Rang , P-containing rock series are mainly distributed in Shifang and Mianzhu of Sichuan, and secondarily in Lueyang and Mianxuan of Shaanxi and all in the form of a moderate- or small-sized deposit.

The Jinhe deposit is typical of the phosphate rocks in the Mid-Devonian Rang in Sichuan. The orebody has settled down on an uneven ancient erosion surface. Usually there is only one layer with an antapical plate undulating up and down sharply and a flat apical plate, thus making the orebody varying in thickness drastically from 0 to 47 m. Generally it is 6 ~ 12 m thick. Appearing in quasi-stratiform or podiform, it is several to several dozen thousand meters long with an obliquity of 15° – 30° in general and 70° – 80° in some individual sections.

The ore is mainly in the form of sand cutting or rubble, and then metasomatic texture and structured mainly in the shape of rubble, sand or micro-stratum. Their P-containing minerals are mainly of cryptocrystalline-cryptomere francolite, and secondarily (svanbergite) with gangue minerals being mainly hydromica and kaolinite, and secondarily pyrite, chalcedon, organic matter and dolomite. Their average P_2O_5 content is 27% ~ 29%, mean MgO content 0.4% ~ 3%, Fe_2O_3 content 2% ~ 4.6% and Al_2O_3 content 3% ~ 6% (Table 2 – 4). So the phosphate belongs to kiesel in character

Table 2-4 Main contents of chemical elements in Devonian phosphate rock (%)

	Machao tan	Yuejia shan	Majiapin	Svanbergite	Jinjiahe	Hejiayan	Chadian
P_2O_5	29.42	34.08	28.95	25.40*	21.65	23.38	20.67
CaO	40.62	45.95	39.94	12.09	37.46	46.81	34.63
MgO	0.28	0.40	1.44	0.46	3.35	4.55	3.40
CO_2	1.54	1.47	3.16	1.23	8.42	16.72	11.19
Fe_2O_3	4.72	3.20	4.66	1.93	1.51	0.55	1.93
Al_2O_3	4.68	3.06	5.70	11.55	1.76	0.29	1.50
SiO_2	5.55	4.49	4.05	5.74	17.99	3.41	—
F	2.65	3.13	2.54	0.58	1.58	0.56	—

Note: * alkali-soluble

c Metamorphic phosphate deposit

Based on genetic classification, metamorphic phosphate deposits are mainly of regional metamorphic ones. Under the impact of regional tectonic movement and the joint effect of temperature, pressure and magmatic activities, phosphate has undergone recrystallization and recomposition. The transubstantiation, however, varies in degree from age to age and from region to region. When the transubstantiation is strong, cryptocrystalline and colloidal nauruite is recrystallized into coarse grains of fluorapatite, making it easy for beneficiation. And when the transubstantiation is weak, recrystallization is not so common or so strong, crystallization degree and particle size of the minerals does not change much, and nor does the dressability of the ore.

- ***Strongly transubstantiated apatite deposits (STAD)***

This type of deposits are mainly distributed in Hubei, Jiangsu and Anhui, and mostly large- or moderate-sized ones, e.g. Huangmeiling, Jinping and Susong phosphate deposits. Besides in Liaoning and Jilin, there are some moderate- or small-sized deposits.

Every deposit has one to several layers, several dozen meters to several dozen hundred meters in length, 8 to 15 m in thickness and moderate in obliquity and in some individual cases, acute in obliquity. The interlayers and apical and antapical plates are of marble, and schist in individual cases. P-containing minerals in the deposits are fluorapatite, with gangue minerals being mainly calcite, dolomite, muscovite, quartz, feldspar, pyrite, etc.. The ore is often in the form of granule, rod or irregular cube, and structured mainly in the shape of block or band, and rubble in rare case. The P_2O_5 content is 7% ~ 16% in general and MgO content from 3% to 6% (Table 2 – 5).

- ***Weakly transubstantiated apatite deposits (WPAD)***

Phosphate deposits at Bulongtu of Inner Mongolia and Liuyang of Hunan belong to this type, large and moderate in size, respectively. Their ore horizon structure is complicated with multiple layers and interlayers. The orebody appears in quasi-stratiform, podiform or stratiform, stretching over several dozen meters to several dozen hundred meters. As a result of tectonics, obliquity of the orebody varies, with most of the horizons in slow slope. The apical and antapical plates and interlayers are of sandy schist, quartz sandstone or marble. P-containing minerals are mainly of francolite and fluorapatite, with gangue minerals being mainly quartz, sericite and muscovite. The ore is mainly in the form of irregular granule, long rod or pseudo-oolite and structured mainly in the shape of block, laminated striation, rubble, or band. P_2O_5 content of the ore is 7% ~ 13% and in some cases 23%. The ore in the Bulongtu deposit has a high content of R_2O_3 (Table 2 – 5). Being weakly transubstantiated, this type of ore is almost the same as untransubstantiated phosphate rocks in dressability.

Table 2-5 Main contents of chemical elements in metamorphic phosphate rock (%)

	SPAD			WPAD	
	Jinping	Huangmeiling	Susong	Liuyang	Bulongtu
P_2O_5	13.45	10~12	16.17	19~21	8.56
CaO	36.58	17~20	24.74	31.28	10.97
MgO	9.92	2~5	3.26	2.99	1.27
CO_2	23.76	6~12	5.04	21.03	—
Fe_2O_3	2.10	4~5	2.94	4.11	*12.93
Al_2O_3	0.68	0.4~0.7	2.43	5.31	3.99
SiO_2	11.91	31~42	34.80	—	59.00
F	1.32	0.8	1.30	—	0.11

Note: * for FeO

2.1.3. Crystalline nature of the phosphate rock in China

Crystalline nature of phosphate rock determines its reactivity and the effectiveness of direct application of the rock and the one of the partially acidulated phosphate rock produced from it.

It is well known that pyrogenetic and metamorphic phosphate rock are fairly well crystallized, which means that they are quite stable in structure. Therefore, these types of phosphate rocks are not suitable for direct application. The world experience indicates that phosphate rocks that can be used for direct application are of the sedimentary type, because they are generally loose aggregates of microcrystalline with large inner surface. Of course, guano can also be used for direct application. But as far as reserve is concerned, it is much smaller than sedimentary apatite.

Sedimentary apatite rocks, when applied directly, vary sharply in effectiveness, which is generally believed to have something to do with isomorphic replacement of CO_3^{2-} with PO_4^{3-}. The more PO_4^{3-} are replaced, the more effective are the rocks in agricultural use.

It is well known that in the crystal lattices of apatite, $Ca_{10}(PO_4)_6 \cdot F_2$, every ion can be isomorphically replaced. For instance, -Ca^{2+} may be replaced by Mg^{2+} or Na^+, and even by Sr^{2+}, K^+, Mn^{2+}, U^{4+} or Fe^{2+}; -PO_4^{3-}, a tetrahedron, can mainly be replaced by CO_3^{2-} and also may in rare occasions be replaced by SO_4^{2-}, SiO_4^{2-}, AsO_4^{3-}, VO_4^{2-}, CrO_4^{2-} or AlO_3^{3-}; and -F^- can be replaced by OH^- or Cl^-.

As a result, pure fluorapatite is very rare in nature and the fluorapatite deposits discovered are mostly products of the isomorphic replacement.

By taking into account the effect of isomorphic replacement, the formula of sedimentary apatite may be expressed as follows:

$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{2+y}$

The above formula shows:

- When CO_3^{2-} replaces PO_4^{3-}, a negative charge and an oxygen atom are lost. Consequently, to keep electrical neutrality or balance of charge, it is essential to have another positive charge entering into the lattice, which is usually implemented by Na^+ replacing Ca^{3+}. Moreover, the replacement also results in the formula losing one oxygen atom. The vacancy must be occupied by another ion, which is usually F^-. Therefore, y in F_{2+y} is a variable, which is determined by the number of vacant sites oxygen atoms leave. So y is quantitatively related to the isomorphous replacement of CO_3^{2-} and PO_4^{3-} with coefficient being roughly $y = 0.4x$.

From the above formula, it can also be discerned that Mg^{2+} has also entered into the lattice. As it is positively bivalent, its entrance does not cause imbalance of charge.

The product of this isomorphic replacement is termed francolite or carbonate apatite.

The function of this isomorphic replacement is, however, limited. Generally speaking, only 21% can be effected, that is, in the lattices, out of every 6 mol of PO_4^{3-} only 21% can be isomorphically replaced, i.e. 1.26 mol at most.

The isomorphic replacement has a critical impact on the crystalline nature of apatite, thus affecting effectiveness of direct application of the rock. The impact is effected on the following aspects:

- Crystals getting smaller;
- Aggregate with more pores;
- Inner surface increased significantly.

Methods are available to roughly calculate degree of the isomorphic replacement. Based on large volumes of data, scientists in other countries state that a_0 axis of the lattice cell is reduced from the original 0.9376nm to 0.9322nm after intensive isomorphous replacement, and so is c_0 axis, which is decreased from 690nm to 687.7nm (standard error: ± 0.0003nm).

By measuring a_0 axis of apatites of different types, x, a and b in the formula of francolite can be worked out in light of the following empirical equation:

$$a_0 = 9.374 - 0.204\ \frac{x}{6-x}$$

As a_0 is known, x can be figured out.

Based on the equation: $a = 1.327\ \mathrm{x}\ \frac{x}{6-x}$

As x is known here, a (number of Na ions replaced in) can be figured out.

Since x is already known, by working on the following equation, b (number of Mg ions replaced in) can be calculated out.

$$b = 0.514 \times \frac{x}{6-x}$$

Once x, a and b are known, it is feasible to work out theoretical formulas of phosphate rock of different types. For instance, in a phosphate deposit in China, the value of a_0 is 9.340 (× 10nm). Based on the above equations, the following can be worked out separately:

$x = 0.8573$

$a = 0.22$

$b = 0.0859$

$y = 0.4\,x = 0.343$

Therefore, the molecular formula of the rocks in the deposit is:

$Ca_{9.694}Na_{0.22}Mg_{0.0859}(PO_4)_{5.143}(CO_3)_{0.8573}F_{2.343}$

Based on the above formula, the molecular weight of the apatite rock is 980.096 and its P_2O_5 content is 37.2%.

Researches demonstrate that there is a clear negative correlationship between a_0 and effectiveness of direct application of phosphate rock powder, that is, the smaller the a_0 value, the higher the degree of isomorphic replacement, and the higher the effectiveness of direct application of the phosphate rock powder.

The Shanghai Academy of Chemical Industry, the Mining Designing Academy of the Ministry of Chemical Industry and the Institute of Soil Science, Academia Sinica committed themselves jointly in conducting measurement and comparison of 80 phosphate rocks samples, of which 78 were from Yunnan, Guizhou, Hubei, Hunan, Sichuan, Jiangxi, Shanxi, Anhui, Hebei and Jiangsu of China and one from Morocco and the other from Kola phosphate deposit of the former Soviet Union. Atomic expressions of the major phosphate deposits are now listed in Table 2 – 6. The closer the atomic expression of a fluorapatite to that of the pure phosphate mineral ($Ca_{10}P_6O_{24}F_2$), the less PO_4^{3-} replaced by CO_3^{2-}, the more stable the lattice of the fluorapatite, the lower the reactivity.

Table 2-6 Atomic expressions of several pure phosphate minerals

General expression	$Ca_{10-a-b-c}Mg_{a}Na_{b}K_{c}P_{6-x}C_{x}O_{24}F_{2+0.4x}$
Morocco deposit	$Ca_{9.75}Mg_{0.01}Na_{0.235}K_{0.0055}P_{5.25}C_{0.76}O_{24}F_{2.76}$
Kunyang deposit	$Ca_{9.85}Mg_{0.03}Na_{0.11}K_{0.018}P_{5.59}C_{0.35}O_{24}F_{2.35}$
Kaiyang deposit	$Ca_{9.83}Mg_{0.011}Na_{0.12}K_{0.007}P_{5.66}C_{0.382}O_{24}F_{2.338}$
Wangji deposit	$Ca_{9.92}Mg_{0.018}Na_{0.028}K_{0.003}P_{5.87}C_{0.13}O_{24}F_{2.12}$
Jinping deposit	$Ca_{9.93}Mg_{0.005}Na_{0.036}K_{0.002}P_{5.984}C_{0.018}O_{24}F_{2.016}$
Koladeposit	$Ca_{9.94}Mg_{0.004}Na_{0.05}K_{0.01}P_{5.993}C_{0.004}O_{24}F_{2}$

Table 2-7 Amount of CO_2 in the lattices of phosphate rocks of different sources

Deposit	CO_2 content in lattice	Type of apatite
Morocco	3.40	High-C fluorapatite
Kunyang, Yunnan	1.50	Low-C fluorapatite
Kaiyang, Guizhou	1.53	Low-C fluorapatite
Wongfu, Guizhou	1.43	Low-C fluorapatite
Wangji, Hubei	0.55	Minimum-C fluorapatite
Jinping, Jiangsu	0.199	Minimum-C fluorapatite
Kola, Russia	0.037	Quasi-fluorapatite

The isomorphic replacement of PO_4^{3-} with CO_3^{2-} changes parameters of the lattice cell, shortening a_0, extending c_0; reducing size of the crystal grain and specific weight of the crystal. These parameters are well correlated with reactivity of the phosphate rock.

The CO_3^{2-} replacement amount (expressed in CO_2) has been recognized as an index of the reactivity of phosphate rocks. In Table 2 – 7, listed are CO_2 replacement amounts of phosphate rocks of 7 sources, 5 from China and 2 from other countries.

Among the phosphate rocks being traded in the world, those coming from Tunisia, Algeria, North Carolina and Morocco are highest in reactivity, with CO_2 content in the lattices being as high as 3.4%. Phosphate rocks from Kunyang of Yunnan, Kaiyang and Wongfu of Guizhou have 1.43% ~ 1.53% of CO_2, being only 40% ~ 45% the CO_2 content in the phosphate rocks from Morocco. These types of phosphate rocks belong to low-C fluorapatite and most of the sedimentary phosphate rocks in China are of such a type. The rocks from Wangji contain 0.55% of CO_2 in the lattices, and from Jinping 0.199%. The two types of phosphate rocks belong to minimum-C fluorapatite and are both of sedimentary metamorphite, with the former being weakly transubstantiated and the latter strongly. The rocks from Kola of Russia have a CO_2 content (0.037%) as low as pure apatite does,

Of the rocks from 78 phosphate rocks deposits in China, an overwhelming majority range between 1.0% and 1.5% in CO_2 content and a few between 1.6% and 2.0%. It also ought to be noted that CO_2 content in the rocks from the same deposit may vary due to difference in horizon position and rock structure. For instance, 7 rock samples from the deposit at Kunyang of Yunnan contain 1.10%, 1.32%, 1.68%, 1.45%, 1.26%, 1.37% and 1.16% of CO_2, individually.

2.2 Phosphate Rock Resources in major Phosphate Producing Regions in the World

In this chapter, a brief introduction will be presented to some major key phosphate producing regions in the world, so as to give readers a synoptical impression. The data cited here are about reserves and volumes of phosphate rocks, different from the statistics about P_2O_5 in Table 2 – 8.

2.2.1. North America

The phosphate rock resources in North America can be sorted into two groups, magmatitic phosphate deposits, often intruded by carbonatite, and cartogenic phosphate deposits of different ages. The former is only distributed in the eastern part of Canada while the latter mainly in the USA, with those in Florida and North Carolina being typical. Both of the groups were formed at the miocene period. In North America, the phosphate mines in Canada with limited output are not so important as those in the USA, so almost all the phosphate rocks Canada consumes are imported from its neighbor.

Phosphate deposits in the USA are mainly distributed in two regions, i.e. Southeast America and West America. Although the permian mines in the west are lower in output of phosphate rocks than those in the southeast, they are quite similar in total reserve. The phosphate rocks from the former, however, are a bit lower in P content and not so easy to dress under the current conditions.

The USA is the largest phosphate rock producer in the world. Since the late 1970s, its output has been fluctuating around 50 million tons (40.87 million tons in 1999), of which 85% are from the Florida region (including North Carolina), 10% from the western states and 4% or so from Tennessee.

The magnitude of the output from Florida is seldom observed in the world. About 25% of its output is exported out of the USA. The phosphate rocks from the western states are sold mainly to Canada (around 10%). Now the reserves of the old mines in Florida are being exhausted, so the mining fields are expanding southward and northward.

2.2.2. South America

The phosphate reserve in South America consists of both igneous deposits and sedimentary deposits of different ages, and both are fairly large in reserve. Presently, the most important phosphate rocks producer in South America is Brazil, whose output, however, can only satisfy half of its own need. Brazil has many types of phosphate deposits, e.g. igneous, sedimentary, guano and aluminum phosphate. The total reserve is estimated at 1,744 million tons.

In terms of phosphate reserve, Peru is the most important country in South America, with an estimated reserve of 6.1 billion tons mainly distributed in the Sechura Desert region in North Peru. The deposits were formed in the Holocene period and are rather complex in structure. The deposits in the desert region show 5.6 billion tons in reserve (on a basis of 30.5% of P_2O_5). Their phosphate rocks are said to be suitable for direct application.

2.2.3. Africa

Africa is the most important phosphate rock producing area in the world and its reserve is also are among the highest in the world. Morocco is the most important phosphate rock producer in the continent and also the first phosphate rock exporter in the world. Other major phosphate rock producers in Africa are Tunisia, Togo, Senegal, South Africa, Egypt and Algeria, with respective annual output exceeding 1.5 million tons.

Except South Africa who produces phosphate rocks mainly for self-consumption, all these African countries export most of the phosphate rocks. In the past few years, some countries, e.g. Morocco and Tunisia, have become aware that the export of finished products earns more money than export of raw material. They begin to cut down export of phosphate rocks if favor of phosphoric acid production destined to export.

The phosphate deposits in Africa are distributed mainly in two parts of Africa, one being northern and western Africa where the deposits are mostly sedimentary and the other southern Africa where the deposits are mainly igneous.

The western part of Africa is rich in phosphate resources. Morocco, in particular, has deposits high not only in reserve, but also in P content. That is why the country has so quickly become a major phosphate rock producer and exporter in the world though it did not start mining its deposits till 1922. In 1999, it exported 21.99 million tons. The total phosphate reserve of Morocco is 40 billion tons, accounting for one quarter of the world's.

Morocco's major phosphate deposits are distributed in a sedimentation zone of the Upper Cretaceous Period and Eocene Epoch, forming an enormous ore belt stretching from northeast to southwest for 350 km. The older is the forming age of the deposit, the lower is its content and the smaller its reserve. The phosphate deposits in this belt accounted for the largest part of the country's total reserve.

The country ranking second in reserve in Africa is West Sahara, whose deposits are all of sedimentary. The ore belt, formed mainly in the Upper Cretaceous Period and Tertiary Period, goes from northeast to southwest. Some of the deposits are very high in content, being over 31% (P_2O_5). There is one ore field whose total reserve reaches 1.6 billion tons.

2.2.4. Former Soviet Union

The ex-Soviet Union ranking second in output of phosphate rocks in the world has an estimated reserve of 7 billion tons (or 11 billions from other sources), among the most endowed countries in the world. About 60% of its reserve is buried in the eastern part of Russia and western part of Ural and about 30% in Kazakstan.

Its deposits fall into two major types -- igneous deposits mainly in the Kola Peninsula, close to the

Bering Sea and sedimentary deposits mainly in Kalatu of Kazakhstan.

The reserve of the deposits in Kola is huge. As they are of the magmatitic type, they do not contain any carbonate, quite similar to those of the same type in South Africa and Brazil. Recently, magmatitic type of phosphate deposits has also been found in Siberia.

Sedimentary phosphate rock deposits, widely distributed in ex-Soviet Union and varied in forming age, are high in total reserve but generally low in content (20% and below, P_2O_5), with the deposit in Kalatu being typical of the type.

2.2.5. Asia and Oceania

Regarding the phosphate resources in Asia and Oceania, the two regions are globally speaking fairly rich. Currently, the total output of phosphate rocks of the two regions accounts for around 9% of the world's total. However, the distribution of the already discovered phosphate deposits is extremely uneven between the countries, and so it is within a given country. For instance, in China, phosphate deposits are concentrated in a few provinces in the southwest part of the country. In Australia, though its reserve is huge, uneven distribution makes it difficult to exploit so that its output remains very small.

As a result of uneven distribution, quite a number of countries in the two continents have not yet discovered any phosphate deposits or have just found deposits very small in reserve. Pakistan, Sri Lanka, Bangladesh, Myanmar, Thailand, Indonesia, Laos, Cambodia, the Philippines and Japan are among these countries.

Important phosphate deposits in the region are mainly distributed in China, India and Oceania. But the output of phosphate rocks differs sharply from country to country.

2.3 Phosphate Rock Reserves in the World and in China

2.3.1. Phosphate rock reserves in the world

The estimation figures of the world's reserve of phosphate rocks vary drastically. One reason is that different sources use different standards for calculation and another is that it is really hard to make any accurate calculation as far as reserve is concerned. Moreover, new deposits are being discovered year after year. Therefore, discrepancy does exist in data of different years from different sources and sometimes it could be very large. Here the data are cited from a report (Pierre, 1993) of the British Association of Fertilizers. Calculated on the basis of P_2O_5, the data are much more specific than those on the basis of orebody. And moreover, the data are more complete (Table 2 – 8).

The author of the monograph above reckons that on the basis of the output of phosphate rocks in 1992, the world's reserve of headings may last 200 years and the potential reserve 400 years and what is more, new deposits are continually being discovered all over the world. The author also holds that South and North Carolina of the USA, Angola, New Zealand and East Siberia are the most promising areas where large-size phosphate deposits may be found.

2.3.2. Phosphate rock reserve in China

According to the 1979 "Criteria for Geological Exploration of Phosphate rock and some other regulations of China, the phosphate rock reserve of China does not include deposits with ore horizons less than 1 m in thickness (on average), phosphate rocks of content below 12% of P_2O_5 (on average) in P-deficient areas or below 15% (on average) in P-rich areas, or apatite below 8% in content. the country's phosphate rock reserve is estimated at 10,848 million tons and 20.36% in P_2O_5 content (on average), of which about 5,600 million tons are of industrial reserve and 5,247 million tons of prospective reserve.

Among the total reserve of the country, 10,115 million tons are phosphate, with an average P_2O_5 content of 20,91%, equal to 7,052 million tons of standard ore(of 30% P_2O_5), accounting for 95.79% of the country's total (7,362 million tons); 643 million tons are metamorphic phosphate rocks, 12.64% in P_2O_5 content and equal to 273 million tons of standard ore, accounting for 3.71% of the country's total; and 83 million tons are endogenic phosphate rocks, 13.33% in content and equal to 37 million tons of standard ore, accounting for 0.5% of the country's total.

Table 2-8 Phosphate rock reserves of the world (million tons P_2O_5)

Continent	Country	Reserve of concentrate	Potential reserve of concentrate	Geological reserve (raw rock)
Europe	Former-Soviet Union	12.7	12.7	69.0
	Belgium			5.4
	Finland	12.7	12.7	42.4
	Greece			4.4
	Italy			6.6
	Norway			5.6
	ex-Yugoslavia			4.8
	Total	12.7	12.7	69.0

Continent	Country	Reserve of concentrate	Potential reserve of concentrate	Geological reserve (raw rock)
North America	Canada	—	21.0	63.7
	USA	369.5	1330.9	8026.0
	Total	369.5	1351.9	8089.7
Latin America	Brazil	87.0	200.2	234.7
	Chile			33.7
	Columbia	1.9	6.3	156.2
	Mexico	3.3	45.0	194.6
	Peru	108.5	108.5	450.4
	Venezuela	10.9	19.5	52.1
	Total	211.7	379.5	1121.9
Africa	Algeria	71.1	71.1	120.0
	Morocco	3639.3	11774.3	15750.0
	South Africa	679.8	680.9	1030.0
	Tunisia	26.9	252.2	480.0
	Total	4491.3	12927.4	17648.5
MiddleEast	Egypt	4.6	156.2	660.0
	Iraq	61.5	601.5	891.0
	Israel	46.8	66.5	260.0
	Jordan	203.3	217.8	440.7
	Saudi Arabia		112.5	1576.0
	Syria	6.3	18.4	177.3
	Turkey	9.0	10.9	42.0
	Total	331.5	1183.7	4094.5
Asia	China	Please refer to Table 2.3.2		
	India	11.8	26.0	38.0
	Vietnam	19.2	32.0	322.0
	Total	2075.9	2192.2	*2278.7
Oceania	Australia	0.7	53.4	614.8
	Christmas	1.8	1.8	59.9
	New Zealand	0.0	0.0	59.9
	Total	6.3	68.1	711.7
World		7751.7	19613.4	29096.1

Note * : The items of "total" include reserves in countries not listed in the table.

2.4 Phosphate Rock Production in the World and in China

2.4.1. Production of phosphate rocks in China

In China the production of phosphate rocks started in Jinping of Jiangsu in 1920, at small scale. By 1949, its cumulative output had not yet reached 0.6 million tons. Afterwards, the production developed rapidly. By 1997 the annual output of the country had soared up to 25.09 million tons (standard ore 30% in P_2O_5). Table 2 – 9 lists annual outputs of China from 1951 to 1997.

China's output of phosphate rocks ranks third in the world, right after the USA and Morocco. Yunnan and Hubei are the major phosphate rock producing provinces in the country.

Among the phosphate rocks produced in China, the rocks from Kaiyang deposits in Guizhou, Dianchi deposits in Yunnan (rubbing beneficiation), Jinping deposits in Jiangsu and Wangji deposits in Zhongxiang of Hubei are all post-dressing headings, and those from other deposits are raw ores of mid-content. The mean content of the phosphate rocks produced in China is 27.41% (P_2O_5). Only 7% of the rocks have content over 30%, 51% of the rocks between 24% and 30% and 42% below 24%.

Table 2-9 Annual outputs of phosphate rocks in China (standard ore, 30% in P_2O_5 million tons)

Year	Output	Year	Output
1951	0.02	1990	21.55
1955	0.08	1991	21.36
1960	1.42	1992	23.20
1965	1.58	1993	21.17
1970	3.94	1994	24.76
1975	10.18	1995	26.54
1980	10.73	1996	22.91
1985	6.97	1997	25.09

Table 2-10 Outputs of phosphate rocks of major producing countries in the world (million tons)

Year		World's	USA	Morocco	Ex-USSR	China
1983	Output	137.417	42.573	19.842	32.40	11.630
	Percent	100	31	14	24	8.5
1985	Output	147.321	50.895	20.779	34.275	
	Percent	100	35	14	23	
1987	Output	153.697	40.954	21.27	37.686	15.165
	Percent	100	27	14	25	9.8
1989	Output	101.129	49.171	18.067	38.00	17.00
	Percent	100	31	11	24	10.6
1991	Output	146.658	48.404	17.90	28.366	21.00
	Percent	100	33	12	19	14.3
1994	Output	128.422	41.555	19.764		26.00
	Percent	100	28	13		17.7
1999	Output	143.41	40.87	21.99		29.00
	Percent	100	29	15		20

2.4.2. Phosphate rock production of the world

Table 2 – 10 shows the outputs of phosphate rocks of the major producing countries in the world and their proportions of the world's total. It could be noted that the world's output of phosphate rocks ranges between 130 and 150 million tons and varies from year to year. It has dropped drastically due to disintegration of the former Soviet Union.

Chapter 3. Production and Consumption of Phosphate Fertilizer in China

Although China's industry of phosphate fertilizers started later, it has been developing rapidly. By 1998, its output had already reached 6.629 million tons (P_2O_5) (Compound P fertilizers and Phosphoric Acid Information, 1999, No. 17, P. 3). Nevertheless, its development has not been a linear one. For instance, in 1985 the output of P fertilizers dropped by 26%, from 2.36 million tons (1984) to 1.758 million tons. In 1993 and 1996, drops of varying extent appeared. The causes of the drops are numerous. No matter what they are, they demonstrate that China will face intensified challenges and competition in the field of P fertilizer production in the world. China must try its best to adapt itself to the new international and domestic situation.

3.1 P Fertilizer Production in China

In Table 3 – 1, are listed data of the production of P fertilizers in China between 1955 and 1998. The rises and falls in the output of every 5 years clearly show the fluctuation of the development of P fertilizer industry of China. This is worth noticing. Of course, on the whole what this industry has achieved is enormous.

In recent years, China ranks second in the world, right after the USA, in the production of P fertilizers (Table 3 – 2). In 1990, the ex-Soviet Union reached its peak in the production, turning out 9.015 million tons (P_2O_5). But after the disintegration of the Union, the output of Russia in 1994 fell down to 1.874 million tons and bounced back somewhat in 1996. Nevertheless, Russia remained the fourth producing country in the world, next to India.

The P fertilizers China produces are mainly of the low-concentration type, such as superphosphate and calcium magnesium phosphate. The total output of the two amounts to 80% of the country's total output of P fertilizers. Now the situation is evolving. For instance, the percentage of high-P-concentration compound fertilizers in the production of P fertilizers rose from 8.3% in 1993 to 11.5% in 1995 (Table 3 – 3). If the item of others (mainly NPK compound fertilizers produced through the installations producing ammonium phosphate) in the table is also counted, the percentage was increased from 8.3% in 1993 to 17.3% in 1997 at a considerable growth rate (it reaches 45% in 2002). But compared to the world's, China has been left far behind others (Table 3 – 4). Table 3 – 4 shows that in some other major P fertilizer producing countries, the output of high-P-concentration compound fertilizers generally accounts for over 70% of the total output of P fertilizers.

Table 3-1 P fertilizer production in China (million ton, P_2O_5)

Year	Output	Increase*	Growth rate (%)*
1955	0.001		
1960	0.193	0.192	
1965	0.688	0.495	25.4
1970	0.907	0.219	5.5
1975	1.531	0.624	10.5
1980	2.308	0.777	8.2
1985	1.758	-0.055	-5.5
1990	4.116	2.358	17.2
1995	5.10	0.424	2.0
1996	5.75		
1997	6.408		
1998	6.629		

* growth for period of five years

Table 3-2 Outputs of the major P fertilizer producers in the world and their ranks (1996)

Country	Output *	Rank	Percentage of the worlds
World	33.80		100
USA	10.50	1	31.1
China	5.75	2	17.0
India	2.62	3	7.8
Russia	1.93	4	5.7

* million tons, P_2O_5

Table 3-3 Major types of P fertilizers and their outputs in China (thousand tons)

P fertilizer	1993		1995		1997	
	Output (P_2O_5)	%	Output (P_2O_5)	%	Output (P_2O_5)	%
Superphosphate	3078	73.8	3914	63.3	4182	65.2
Ca.Mg.phosphate	704	16.9	1205	19.5	912	14.3
Amm.phosphate	242	5.8	551	8.9	886	13.9
TSP	55	1.3	100	1.6	139	2.2
Nitric phosphate	51	1.2	61	1.0	79	1.2
Others	38	0.9	356	5.8	210	3.2
Total	4168	100	6186	100	6408	100

Table 3-4 High-concentration P fertilizers in some countries (1994)

Country	Total output of P fertilizers (million tons P_2O_5)	Percentage of high conc. P fertilizers
USA	10.223	69.1
India	1.874	80.7
Ex-Soviet Union	8.867	76.1
France	0.697	92.2

3.2 Consumption of P Fertilizers in China

Listed in Table 3 – 5 are consumptions of P fertilizers during the years after 1995 in China. In the early 1950s little was consumed (210,000 tons, P_2O_5), and that in the mid 1990s' the consumption of P fertilizers had reached 6.894 million tons (P_2O_5), about 328 times as much as in the 1950s. The data in Table 3 – 6 show variation of the proportion of China's consumption of P fertilizers as referred to the world consumption. It is clear that in 1949 it was null while in 1994 it accounted for 27.8% of the world's. Today, China has become the biggest consumer in the world (Table 3-7). Although the USA is the biggest producer of P fertilizers, its consumption is lower than China's, ranking second in the world.

China thus ranks first in consumption of P fertilizers, but its consumption per unit area is not the highest in the world. (Table 3 – 8).

The data in Table 3 – 8 show that in terms of P fertilizer consumption per unit area, China is higher above the world average and very near from France, but much lower than Japan and the Netherlands.

Table 3-5 Annual consumption of P fertilizers in China (1995-2001), million tons of P_2O_5

Year	Consumption
1995	10.35
1996	11.00
1997	11.68
1998	11.77
1999	12.25
2000	12.41
2001	12.74

Table 3-6 P fertilizer consumption in China and in the world (million tons, P_2O_5)

Year	China	World	Proportion (%)
1949	-	5.40	-
1963	0.186	10.40	1.8
1970	0.991	18.50	5.3
1978	1.974	28.28	7.0
1994	8.006	28.81	27.8

Table 3-7 Major P fertilizer consumer in the world (1994, million tons, P_2O_5)

Country	Consumption	Ranking
World	28.813	
China	8.000	1
USA	4.102	2
India	2.670	3
France	1.014	4
Russia	0.900	5

Table 3-8 P fertilizer application rate in some countries (kg/ha, in 1993)

Country	Fertilization rate ($N + P_2O_5 + K_2O$ kg/ha)	P application rate (P_2O_5 kg/ha)
World	89.9	21.5
China	270.5	59.8
USA	109.6	22.1
France	252.6	55.5
Germany	220.5	34.3
Russia	29.7	6.9
India	74.3	16.1
Japan	451.5	180.9
Netherlands	577.3	74.0

Note: Calculation based on FAO "Fertilizers Yearbook" 1994.

The Statistics of the recent years show that China consumes about 12-7 million tons of P fertilizers (P_2O_5) a year (It is a rough estimation including compound fertilizers for which NPK ratio is not indicated). In the past, the acreage of cultivated land in China used for calculation was set at 95.333 million ha. Based on the findings of the second national soil survey, the acreage of cultivated land is determined to be 133.333 million ha. Taking into account the multi-cropping index of 1.56 or so, the actual cropped area of the country should be around 208 million ha. Based on the three figures, the P fertilizers consumption per unit area is calculated to be:

- 134 kg (P_2O_5)/ha on the basis of 95.333 million ha of cultivated land;
- 95 kg (P_2O_5)/ha on the basis of 133.333 million ha of cultivated land; and
- 61 kg (P_2O_5)/ha on the basis of 208 million ha of cultivated land.

Consequently, the actual application rate of P fertilizers is not high in China.

3.3 Issues in P fertilizer production in China

Issues discussed here are raised from the view angle of agriculture, and hence have nothing to do with P fertilizer industry. For instance, the most important problem is the shortage of high quality phosphate rocks, which has already been addressed in Chapter 2. It is not necessary to talk about it again here. This part will deal with two questions.

3.3.1. The output of P fertilizers still inadequate to meet the need of the agricultural production

In the past 40 years, the output of P fertilizers in China has been growing at an annual rate of 21.1%. Yet, it is still inadequate to meet the need of the agricultural production. The gaps between the output and the consumption of P fertilizers are listed in Table 3 – 9. As the output is much lower than the consumption, China has to import a considerable amount of P fertilizers (Table 3 – 10).

Table 3-9 Gaps between the output and consumption of P fertilizers in China (1981 ~ 1995, million tons, P_2O_5)

Year	Output (A)	Consumption (B)	Shortage (A – B)
1981	2.508	3.143	-0.635
1983	2.666	3.798	-1.132
1985	1.758	3.702	-1.944
1987	3.239	4.407	-1.148
1989	3.663	5.114	-1.453
1991	5.921	6.334	-0.413
1993	4.168	7.496	-3.328
1995	6.186	10.4	-4.16
1997	6.400	11.7	-5.3

Table 3-10 Import of P fertilizers to China (1981 ~ 1997, million tons, P_2O_5)

Year	Import	% of the consumption
1981	0.436	13.9
1983	1.029	27.1
1985	0.900	24.3
1987	1.166	26.5
1989	1.554	30.4
1991	2.838	44.8
1993	2.450	32.7
1997	2.593	22.2

It is clearly shown in Table 3 – 10 that China increased its import of P fertilizers from 0.44 million tons in 1981 to 2.59 million tons, around 22% of the total consumption, in 1997.

3.3.2. Dominance of low-concentration P fertilizers in production

Today, the production of P fertilizers in the world has been oriented towards high- concentration types. The mean concentration of fertilizers in other countries is around 40%, but China's remained to be 22% in 1994. The mean concentration of its N fertilizers was 24% whereas that of its P fertilizers is only 15%. This is just because the P fertilizers China produced were still dominated by low-concentration types. As it is shown in Table 3 – 3, the output of superphosphate and calcium magnesium phosphate accounted for 90.7% of the total output of P fertilizers in 1993. Although this share decreased somewhat in 1995, it still remained at 82.8%. Now the Ministry of Chemical Industry has been taking positive measures to change the situation. During the period of 1996 ~ 2000, great efforts were devoted to building up large- and moderate-scale installations to produce high-P-concentration compound fertilizers. By 2000, China will have built up 18 high-P-concentration fertilizer plants, among which 5 will produce double superphosphate, 10 will produce ammonium phosphate and 3 will produce nitric phosphate. In addition, the existing 94 small-scaled ammonium phosphate and double superphosphate plants will have been revamped with improved capacity totaling 3 million tons of high-P-concentration fertilizers. Thus, the production capacity for high-P-concentration fertilizers will account for 40% of the total capacity for P fertilizers (Zeng Xiankun, 1994). The percentage of high-P-concentration fertilizers against the total of P fertilizers rose from 8.3% in 1993 to 17.3% in 1997.

Chapter 4. Direct Application of Rock Phosphate: Basic Experience of China

To solve the problems of the shortage of P fertilizers and low grade of the phosphate rocks, China began to study direct application of phosphate rock powder very early in the 1940s. Following is the basic experience of China in this aspect.

4.1 Crop response to phosphate rock powder in relation to properties of the soil, characteristics of the plant and quality of the phosphate rock

In China direct application of phosphate rock powder started as early as in the 1940s. In the 1950s and 1960s, large-scale nation-wide studies and experiments in this field were conducted. In the 1970s it was being extended all over the country and in the peak period, the area under the related experiment reached a total as large as 6700 ha. However, from the 1980s onwards, the area has fell down to a very limited figure.

Decades of experience (Li Chingkwai, et al. 1992) demonstrate that for direct application of phosphate rock powder, it is essential to choose proper soils, proper crops and proper phosphate rocks or no obvious crop response would be observed (Jiang Baifan, 1988).

4.1.1. Effect of soil properties on crop response to phosphate rock powder

Soil properties of the land where phosphate rock powder was directly applied have great impact on crop response to the application. Phosphate rock powders of the same source may have utterly different crop responses on soils different in properties. The main factor affecting decomposition of phosphate rock powder is soil acidity. Experiments of applying artificially prepared radioactive phosphate rock powder (from Kunyang) into three soils different in acidity were conducted with results showing that in the plot of acid soil with pH5.3, 86% of the P absorbed by the plant was from the phosphate rock powder and only 14% from the soil and crop response was extremely significant; in the plot of slightly acidic soil with pH5.8, 52% from the phosphate rock powder and 48% from the soil and significant crop response; and in the plot of calcareous soil with pH8.6, only 35% from the phosphate rock powder and 65% from the soil and insignificant crop response. Based on theoretical calculation, the equation of the correlation between soil pH and reactivity of phosphoric acid ions when apatite was in the soil solution goes as: $pH_2PO_4^- = 2pH - 5.18$. It could be inferred from the equation that the lower the soil pH, the easier the decomposition of phosphate rocks. Observation of the change in P form in the soil may also support the argumentation. Half a year after phosphate rock powder from Kaiyang was applied into an acid soil with pH5.0, half of the P elements in the powder were decomposed off and turned into ferric phosphate and aluminum phosphate, while in a paddy soil with pH6.1 the decomposition rate was very low and the total P transformation rate remained below 10% even after 2 years. The curve of P dissolving from phosphate rock powder into buffer solution different in pH also shows that P in the solution significantly increased with the decrease in pH of the solution.

Production practices also indicate that direct application of phosphate rock powder in P-deficient soils with pH below 5.5 will generally meet certain crop response in yield.

4.1.2. Plants capability of absorbing P from phosphate rock powder

Plants capability of absorbing P from phosphate rock powder varies from crop to crop in the same soil applied with the same phosphate rock powder. Over 30 years, a large number of field experiments, pot experiments and extension-oriented demonstrative experiments were carried out one after another in major types of soils in Guangdong, Guangxi, Zhejiang and Jiangsu Provinces. As the experiments lasted for years, different weather conditions of different years had some impact on absolute yield of the crops. Therefore, in calculation, the yield from the plot applied with superphosphate or calcium-magnesium phosphate was taken as the base of 100, and the phosphate rock powder moderate in reactivity as benchmark. When P- absorbing capabilities of plants are expressed in mean percentage of relative increment against the base, they can be roughly divided into the following types:

- Crops with strong P-absorbing capability: radish, rapeseed, buckwheat, common vetch, pea, and some other tropical green manure crops. In the current year of direct application of phosphate rock powder, their crop response could reach 70% ~ 80% (as is against the yield of the crop applied with chemical P fertilizer).
- Crops with moderate P-absorbing capability: soybean, rice bean, milk vetch, peanut, striped Crotalaria, Sesbania, corn, potato, sesame,

bicolor lespedeza, etc.. Their relative crop response varied between 40% and 70%;

- Crops with weak P absorbing capability: millet, wheat, rye, rice, etc.. Their relative crop response ranged between 15% and 30%.

Among the above-mentioned green manure crops, leguminous green manure crops, in particular, had fairly strong P absorbing capability. Direct application of phosphate rock powder on these crops did not only gives significant crop response, but also contributed much to higher yield of the following rice crop. In South China, direct application of phosphate rock powder on rubber trees had crop response in yield 1/2 ~ 2/3 of what superphosphate gave in the first three years and then the crop response of the former became more than twice as much as that of the latter in the following 5 years, which indicated that phosphate rock powder had a long period of residual effect. In long-term experiments with crops, similar results were also found.

4.1.3. Crop response in relation to characters of the crystal of apatite

Characters of the crystal of apatite are the inner factor that determines how effective direct application of phosphate rock powder would be. Direct observation through electronic microscopy revealed that phosphate rocks highly effective in direct application were often poorly crystallized and loosely structured appearing like foam, with crystal grains 0.5μm or below in size. This type of phosphate rocks are of sedimentary deposit, for instance, eluviation cave cumulus phosphate or bio-cumulus phosphate. The karst cave phosphate in Guangxi and the guano in Xisha Isles are representative of the type. All phosphate rocks with low effectiveness in direct application were often found to have hexagonal crystal sheets with distinct corners. The crystals were compactly structured and 3 ~ 10 μm in size. The geological attitude of this type of phosphate was of magmatite or metamorphite. For instance, the metamorphic phosphate deposits in Jinping of Jiangsu and Feidong of Anhui are of such a type. Phosphate rocks with direct application effectiveness ranging between the two had distinct crystals without distinct corners and size of the crystals ranged between 0.5 and 3 μm. Most of the phosphate deposits in China belong to this type and are often phosphate rocks of marine and terrestrial sediments. On x-ray diffractometry, diffraction peak is related to crystallization degree of apatite. When the ratio of half-peak width vs peak height of the dominant peak is taken as an index, the higher is the ratio, the higher is the effectiveness of direct application of the phosphate rock.

Research findings show that, whatever sources of phosphate rock, magmatite, metamorphite or sedimentary, the major typical mineral of calcium phosphate is fluorapatite. However, during the forming process of sedimentary, fluorapatite may undergo a series of isomorphous replacements under the influence of different geological conditions. The replacement of PO_4^{3-} tetrahedrons with CO_3^{2-} and F exerts most impact on the properties of apatite. A study was conducted on 101 phosphate rock samples, of which 99 were typical from China and one from

Morocco and the other from Russia. The one from Morocco was of sedimentary and very effective in direct application, whereas the one from Russia was of magmatite and much less effective. Results of the study reveal that the replacement amount of PO_4^{3-} with CO_3^{2-} is closely related to crystal characters and chemical properties of apatite and effectiveness of direct application of the phosphate rock powder. The replacement amount of CO_3^{2-}, when expressed in CO_2 %, of the mentioned 101 samples, ranged between 0.04% and 3.62%. With the increase in CO_2 %, a_0 axis of lattice cells (horizontal axis) decreased from 0.9380 to 0.9331 nm; Da_0 (extension in the direction of a_0 axis) from 224.1 to 39.1 nm; and Dc_0 (extension in the direction of c_0 axis) from 200.0 to 42.4. Statistical analysis of the results from biological tests obtained from 21 samples out of the 101 indicate that the crop yield increase rate or the crop P uptake are positively related to CO_3^{2-} replacement amount and negatively to parameters of lattice cells, i.e. a_0, Da_0 and Dc_0 (with significance level reaching $P \leqslant 0.001$). All phosphate rocks with high CO_3^{2-} replacement amount are also highly effective in direct application. The sedimentary deposits in Daxin and Debao of Guangxi, Fengtai of Anhui, Kunyang and Jinning of Yunnan, Kaiyang of Guizhou and Zhaoyang of Jiangxi are typical of this type of rocks. Phosphate rocks with low CO_3^{2-} replacement amount are also low in effectiveness of direct application. The metamorphitic phosphate deposits in Huangmei and Huangpo of Hubei, Feidong of Anhui and Jinping of Jiangsu are typical of this type. Generally phosphate rocks of marine or terrestrial sedimentary phosphate rocks are in between the two in effectiveness of direct application. Statistical analysis by progressive regression also indicates that among the parameters of the lattice cells, Da_0 and Dc_0 are the most important factors leading to higher yield of crops, that is, size of the crystals of fluorapatite determines effectiveness of direct application of the phosphate rock powder. These results comply with theory.

- The CO_2 index acquired by means of infrared spectroscopy (the ratio between C-O and P-O bonding strength) is also closely related to the CO_2 % in apatite and results of the biological experiments at an extremely significant level. Its correlation coefficient with the former is $r = 0.926$ ($P \leq 0.001$).
- The relationship between the chemical properties of apatite and the effectiveness of phosphate rock powder is reflected mainly in solubility of the rocks. In China, the 2% citric acid method is often used in the experiments and research works in this field. However, when the phosphate rocks have a high content of carbonate minerals, results obtained from this method are biased, more often by calcite than by dolomite. If the rocks are pretreated or extracted twice with 2% citric acid, and only the P extracted in the second time is measured, the kind of bias is significantly alleviated and it's the correlation of its outcomes with results of biological experiments is twice or more as reliable.

- If an apatite sample is extracted with 2% citric acid again and again, the amount of P extracted each time is quite approximate to each other. It seems to show that the extraction process is similar to the process of chemical extraction. The amount of P extracted varies from sample to sample. This is because they differ from each other in crystal characters. Out of phosphate rocks with high effectiveness in direct application, each extraction can extract about one-third of the total P content in the rock and three times of extraction may extract almost all the P in the rock. Out of phosphate rocks with low effectiveness in direct application, each extraction can extract only about 10% or even less. Such a variation is closely related to the effectiveness of direct application of phosphate rock powder
- On acid soils under the same conditions, biological experiments were conducted with results showing that the amounts of P extracted from phosphate rocks with 2% citric acid, excluding those with too much carbonate minerals, were related to relative increases in crop yield in such a pattern: phosphate rocks with P_2O_5 extraction rate exceeding 6% may increase the yield by 60% relatively; those with the rate ranging between 6% and 3%, by 60% to 30%; and those with the rate below 3%, by 30% or below.

4.2 Global Evaluation of Effectiveness of 45 Kinds of Phosphate Rock Powders from China (Evaluation of Crop Response in Yield)

In order to avoid influence of difference in experiment conditions on effectiveness of phosphate rock powder in direct application, the Institute of Soil Science, Academia Sinica (Shi Zhengyuan, et al. 1982) performed a global evaluation of the effectiveness of phosphate rock powders made out of 45 kinds of phosphate deposits from China. The so-called global evaluation is to conduct the experiment on crop response to the phosphate rock powders under the same conditions, i.e. the same soil (red soil derived from the Quaternary red clay, pH4.5), the same crop (buckwheat) and the same field management and fertilization practices. Fig. 4 – 1 shows the sequence of the phosphate rocks in crop response. Based on the sequence, the 45 deposits can be divided into three categories: high, moderate and low in effectiveness.

Yield increase rate (%)

$$=\frac{\text{Yield..with..PRP} - \text{Yield..without..P}}{\text{Yield..with..Ca.Mg.P} - \text{Yield..without..P}} \times 100$$

Therefore, the yield increase rate is a relative one with the yield increment of the application of Calcium-Magnesia-Phosphate as basis, 100.

Phosphate rocks with high crop response: Phosphate rocks in this category will have crops increase yield by over 60%. There are altogether 13 kinds of phosphate rocks. Generally speaking, to produce phosphate rock powder phosphate rocks in this category are the priority choice. However, there are several noteworthy issues: a) When the production of chemical P fertilizers compete for the raw material, it must have the priority; b) Among the 13 kinds of phosphate deposits of this category, two are ideal for direct application, that is, Karst cave type and the low grade phosphate rocks but high in direct application effectiveness, for instance, phosphate rock Sample No. 81 from Yulin of Guangxi, and Sample No. 65 from Mianzhu of Sichuan. These two kinds of phosphate rocks could not be subject of competition between direct application and chemical P fertilizer industry, because they are either low in grade or widely scattered in small reserve; and c) It was found during the experiment, phosphate rocks from different orebodies in the same orefield could differ drastically in direct application effectiveness. For example, Rock Samples No. 63, No. 64 and No. 65 are from the same location, Mianzhu of Sichuan, but they belong to three different categories, high, moderate and low., separately. It is obvious that they will be used for different purposes. For instance, Sample No. 65, which is low in grade but high in direct application effectiveness, ought to be used for direct application; that of Sample No. 63, which is high in grade but moderate in effectiveness, ought to used as raw material to produce chemical P fertilizers; and that of Sample No. 64 (svanbergite), which is low in both grade and effectiveness, ought to be exploited for specific utilization.

Phosphate rocks with moderate crop response: In this category, altogether 20 kinds of phosphate rocks, when directly applied in the form of powder, can increase crop yield by 30% ~ 60%. Those high in grade ought to be used for fertilizer production as much as possible.

If they are to be used for direct application, it is better in the areas close to their deposits and in farmlands with favorable soil and crop conditions. Therefore, phosphate deposits, such as Samples No. 17, No. 21 and No. 43, whixh derived from areas with neutral and particularly calcareous soil should not be used for direct application.

Phosphate rocks with low crop response: The phosphate rocks in this category can only increase crop yield by 30% or less when used as phosphate rock powder. There are altogether 12 samples. On normal conditions, they are not fit for direct application. Most of the phosphate rocks are of metamorphic, which is easy to dress. So even if they are low in grade, they can be used for production of chemical fertilizers.

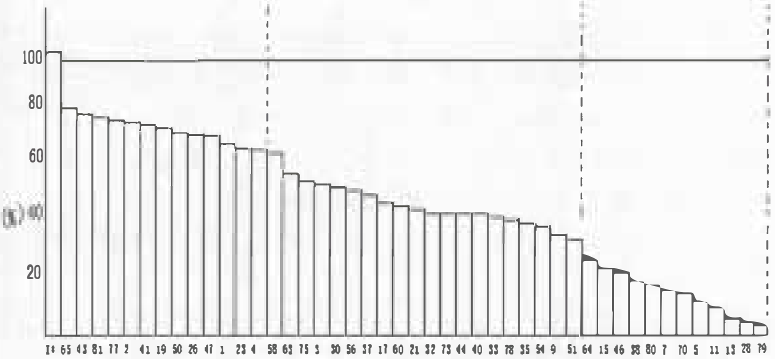

Fig. 4 – 1 Relative effectiveness of phosphate rock powders out of 45 kinds of phosphate rocks (figures in the x axis correspond to the numbers attributed to locations of sampling)

Chapter 5. Conditions for and prospect of development of PAPR in China

In the four previous chapters, the background of production and utilization of PAPR in China has been elaborated. This chapter will further talk about prospect of production and utilization of PAPR in China.

5.1 Acid Soils in China and their Available P

Research works indicate that in P-deficient acid soils crop response to PAPR is the best, though in some neutral soils, sometimes it can also be good. Consequently, acreage of acid soils and soils deficient in P of a country is an important premise for adoption of PAPR. In China, acid soils are mainly distributed in the tropical and subtropical regions of the country. They are chiefly latosol (pH4.5 ~ 5.5), lateritic red soil (pH4.5 ~ 5.5), red soil (pH4.5 ~6.0), and yellow earth (pH4.5 ~ 5.5). Besides, yellow brown earth (pH5.0 ~6.0) in the central part and bleaching podzol (pH4.5 ~6.0) in the northern part and acidic sulfatic soil in the southern part of China are all in the category of acid soil. In the following paragraphs discussion will be devoted to the four types of soils (Xi Chengfan, 1998).

5.1.1. Latosol

It is mainly distributed in the northern boundary zone of the tropical region, south of 20^o Lat. N, including the Hainan Island, Leizhou Peninsula and part of Guangxi, Yunnan and Taiwan, and totaling 3.93 million ha (Taiwan exclusive), about 0.45% of the country's total area. The acreage of latosol in the Hainan Island accounts for 56.1% of the country's total, in Guangdong for 16.6%, in Yunnan for 15.7%, in Guangxi for 6.4% and in Xizang for 5.2%.

Latosol is one of the soils that are the most deficient in available P. In Table 5 – 1 listed are total P and available P levels in the latosols in Guangdong and Hainan (Xi Chengfan, 1998). It is clear that in the two provinces, latosols of whatever parent materials are low in both total P and available P. Although in some latosols derived from basalt and sandstone total P sometimes exceeds 0.1%. It should be noted that total P and available P in latosol may grow due to the fact that P input exceeds P removal, leading to building up of soil total P, especially available P.

5.1.2. Lateritic red soil

Being actually a transient kind of soil between red soil to latosol, it spreads extensively between 22^o and 25^o Lat. N. and on the northern side of the line that goes from Fuqing to Huaan of Fujian, to Dapu, Meixian and Heyuan of Guangdong, to Qinzhou Gulf of Guangxi, to Weishan and Baoshan of Yunnan. It covers southeastern part of Fujian, southeastern part of Guangdong, southern and southwestern parts of Guangxi, southwestern part of Yunnan, central western part of Hainan and southern part of Taiwan. Tracts of laterite can also be found in Sichuan. Its total acreage is 17.787 million ha, accounting for 2.18% of the country's total land area and 6% of the country's total area of cultivated land. About 37% of it is in Guangdong, 29% in Yunnan, 22.2% in Guangxi, 3.6% in Fujian, 1.9% in Hainan, 6.1% in Xizang and 0.2% in Sichuan (Taiwan exclusive).

Lateritic red soil is also one of the P-deficient soils in

China. Generally, available P content in the soil is lower than 10 mg/kg · P. Table 5 – 2 shows P in natural and cultivated lateritic red soils in some major provinces.

Table 5-1 P levels in latosols of different parent material

Parent material	Province	No. of samples	Total P(%)	Available P(mg/kg)
Basalt	Hainan	90	0.18	5.3
	Guangdong	16	0.07	2.0
Granite	Hainan	222	0.06	6.7
	Guangdong	19	0.185	4.0
Sand shale	Hainan	176	0.056	5.5
	Guangdong	30	0.133	9.8
Shallow marine deposit	Hainan	140	0.042	4.0
	Guangdong	13	0.036	2.0

Table 5-2 P in lateritic red soils

Province	Landuse	Total P (P%)	Available P (mg/kg · P)
Yunnan	Natural	0.064	4.7
	Cultivated	0.094	9.7
Hainan	Natural	0.064	9.4
	Cultivated	0.090	7.2
Sichuan	Natural	0.049	
	Cultivated	0.061	7.6
Guangdong	Natural	0.047	4.1
	Cultivated	0.056	17.3
Fujian	Natural	0.061	1.3
	Cultivated	0.054	7.2

From Table 5 – 2, it is clearly discerned that the available P levels of most of the soils are in the range of deficiency (<10 mg/kg · P), and those of the natural soils in Yunnan, Guangdong and Fujian are all in the range of extreme deficiency (<5 mg/kg · P).

5.1.3. Red soil

It is mainly distributed in the low-mountaineous and hilly regions in the provinces on the south of the Yangtze River, covering most parts of Jiangxi, Fujian, Zhejiang and Hunan, the northern parts of Guangdong, Guangxi and Yunnan, and the southern parts of Jiangsu, Anhui, Hubei, Guizhou, Sichuan and Xizang (Table 5 – 3). With its total acreage being 56.902 million ha, it amounts to 6.5% of the country's total land area.

Table 5-3 Distribution and areas of red soil in some major provinces (million ha)

Province	Acreage	Percentage	Areas of distribution
Yunnan	11.370	32.3	Central part, surface of the plateau, mid- & low-hills
Jiangxi	10.531	70.7	Low mound and hilly regions
Hunan	8.638	51.0	Low mound and hilly regions
Fujian	7.681	62.5	Hilly regions in NW, E and central parts
Guangxi	6.549	40.6	Low mound and hilly regions
Zhejiang	3.872	40.0	Low mound and hilly regions

Red soil is also one of the seriously P-deficient kinds of soils in China. Table 5 – 4 shows P in subtypes of red soil.

Table 5-4 P status in the subtypes of red soils

Subtype	Number of samples	Available P (mg/kg · P)
Red soil	36	3.6
Yellow red earth	15	2.6
Brown red earth	12	1.8
Lateritic soil	4	7.4
Total	67	(mean value) 3.3

Table 5 – 4 shows that the soils in the red soil regions are extremely deficient in P (<5 mg/kg · P). Of 67

samples of red soils the mean value is only 3.3 mg/kg·P. It is, however, noteworthy that it is over 20 years since the Second National Soil Survey was conducted. As in these regions, farming practices have been bringing farmland nutrient balance towards gaining (Lu Rukun, et al. 2000), soil available P in the farmland is getting higher. For instance, the studies we did in two typical regions demonstrated that in Jinhua County of Zhejiang Province, the soil P gained 101% in balance, during the four years of 1993 ~ 1997, the soil available P rose by 16%, from 12.1 mg/kg·P to 14 mg/kg·P. And in another region, Honghu Township, Yujiang County of Jiangxi Province, in the period from 1983 to 1997 soil P in the farmland gained 137% in balance and soil available P increased by 125%, from 8 mg/kg·P to 18 mg/kg·P.

5.1.4. Yellow earth

It is an acid soil in the humid subtropics with pH lower than that in red soil. As it contains much hydrated iron oxide (geothite, limonite), it appears yellow, which is related to its development environment, which is foggy and humid without distinct dry and wet seasons.

The acreage of yellow earth in China is 23.24 million ha, which is mainly distributed in Guizhou province. Of the 7.04 million ha of yellow earth in Guizhou, about 46.2% or 1.55 million ha are upland fields. Table 5 – 5 lists the distribution and acreage of yellow earth in some major provinces.

Table 5-5 Distribution of yellow earth in China

Province	Acreage (million ha)	Percentage (%)
Guizhou	7.038	30.27
Sichuan	4.522	19.46
Yunnan	2.295	9.87
Hunan	2.107	9.06
Xizang	1.970	8.48
Guangxi	1.273	5.48
Zhejiang	1.029	4.42
Guangdong	0.872	3.78
Fujian	0.878	3.75
Total	23.247	100

Available P in yellow earth is generally below 10 mg/kg·P, so it is a P-deficient type of soil. In the provinces where yellow earth is mainly distributed, the acreage of farmland deficient in P is also quite large. For instance, 90% of the farmland in Sichuan is deficient in P, 74% in Guizhou, 53% in Yunnan, 74% in Hunan, 83% in Guangxi, 78% in Zhejiang, 73% in Guangdong and 40% in Fujian. Of course, in recent years the proportions of P-deficient farmland have been changing significantly, showing a declining trend of varying degree. The above-listed figures, however, reveal the seriousness of the issue of P deficiency.

5.2 P adsorption of Red Soil in China

As some research workers reported that in soils with high P adsorption or fixation capacity PAPR gave good crop response (Chien et al, 1988) (Its mechanism will be discussed in the next chapter), soil P adsorption capacity will be an important factor influencing effectiveness of PAPR. Therefore, a brief introduction will be presented about the research and findings the Institute of Soil Science, Academia Sinica obtained in this field (Shi Zhengyuan et al. 1998).

The experiment had altogether 111 soil samples, of which 30 were gathered from Jiangxi, 30 from Hunan and 51 from Zhejiang.

5.2.1. P adsorption or fixation capacity of red soil

The mean P adsorption capacity of the 111 soil samples (80 of surface soil and 21 of subsoil) was 408.3 mg/kg·P. The mean P adsorption capacity of the 80 surface soil samples was 393.8 mg/kg·P. Among the 80 samples, 48 were from upland with a mean P adsorption capacity of 409 mg/kg·P and 32 from paddy fields with a mean P adsorption capacity of 371 mg/kg·P. The mean P adsorption capacity of subsoil samples (including paddy and upland) was 657.9 mg/kg·P. No matter whether it is surface soil or subsoil, their P adsorption capacity varied greatly. For instance, the P adsorption capacity of upland surface soil ranged between 58 mg/kg·P and 1297 mg/kg·P, and the one from paddy surface soil between 91 mg/kg·P and 1002 mg/kg·P. Such huge variation may clearly show itself up in the coefficient of variability of the mean values. For instance, the CV obtained were 76.5%, 59.3% and 57.8% respectively for upland surface soil, paddy surface soil and subsoil.

To give readers a clear picture, Table 5 – 6 lists the distribution of P adsorption capacities of the 111 soil samples. It is clearly shown that soil samples with P adsorption capacity ranging from 0 to 400 mg/kg·P accounted for about half, from 400 mg/kg·P to 800 mg/kg · P for 30% and beyond 800 mg/kg · P for 20% of all the samples.

Based on the above data, P adsorption capacities of red soils can be roughly divided into three grades: low (0 ~ 400 mg/kg · P), medium (400 ~ 800 mg/kg · P) and high (above 800 mg/kg · P).

Table 5-6 Distribution and grading of P adsorption capacities of red soils

Grade	Capacity (mg/kg · P)	Number of samples	Percentage
Low	0 ~ 200	29	26
	201 ~ 400	29	26
Medium	401 ~ 600	21	19
	601 ~ 800	13	12
High	801 ~ 1000	8	7
	> 1000	11	10

5.2.2. Factors influencing P adsorption capacity of red soil

From the huge variation of P adsorption capacity of red soil, it is known that there are quite a number of factors that may influence P adsorption capacity of red soil. The following is devoted to discussing some of the influencing factors.

- ***Parent material***

From the data in Table 5 – 7 it can be observed that red soil and Lateritic paddy soil derived from granite are the lowest in P adsorption capacity among soils derived from three different parent materials while red soil and paddy soil developed from the Quaternary red clay, limestone and chalkstone have the highest adsorption, which is believed to be related to the light texture of the soils derived from granite.

Table 5-7 P adsorption capacity of red soils different in parent material

Parent material	Location	Soil	Sampling depth (cm)	P fixation capacity (mg P/kg)
Granite	Ninggang, Jiangxi	Red soil, upland	0~10	198
	Ninggang, Jiangxi	Red soil, upland	0~10	256
	Hengyang, Hunan	upland	0~10	62
	Hengyang, Hunan		0~30	264
	Shuangfeng, Hunan	Paddy soil	0~15	267
	Shuangfeng, Hunan	upland	0~25	272
	Average	—	—	**220**
Quaternary red clay	Ninggang, Jiangxi	Paddy	0~15	438
	Ninggang, Jiangxi	Upland	0~25	752
	Hengyang, Hunan	Upland	—	480
	Hengyang, Hunan	Paddy	—	278
	Shuangfeng, Hunan	Upland	—	331
	Shuangfeng, Hunan	Upland	—	476
	Average	—	—	**459**
Limestone	Ninggang, Jiangxi	Upland	—	540
	Ninggang, Jiangxi	Paddy	—	419
	Hengyang, Hunan	Upland	—	281
	Hengyang, Hunan	Upland	—	471
	Shuangfeng, Hunan	Paddy	—	468
	Shuangfeng, Hunan	Upland	—	215
	Average	—	—	**399**

- ***Depth of soil layers***

Table 5 – 8 shows P adsorption capacity varies with soil depth. Generally, it goes up to a varying extent with soil depth, following a mechanism still unclear. It

may be related to a lower organic matter content and a higher content in soil mineral with the deeper soil layer.. Besides, P adsorption capacity depends mainly on clay content in the minerals. These may explain the phenomenon of P adsorption capacity being higher in the subsoil than in surface soil.

Table 5-8 Effect of soil depth on soil P adsorption capacity

Soil	Sampling site	Depth (cm)	P absorpted (mg P/kg)
Huangjingnitian (paddy soil)	Jinhua (Zhejiang)	0 - 14	264
		14 - 22	251
		> 22	714
	Jinhua (Zhejiang)	0 - 12	403
		12 – 40	821
		40 – 75	941
		> 75	1002
Greyish red soil (upland)	Shuangfeng (Hunan)	0 – 25	215
		25 – 60	459
		> 60	980
Gravely purplish red sady soil (upland)	Jinhua (Zhejiang)	0 – 15	512
		15 – 30	605
		> 30	682
Reddish purple sandy soil	Hengxian (Zhejiang)	0 – 9	33
		9 - 44	536

- ***soil active Fe and Al***

No matter whether soil texture or clay content in the minerals is being considered, they both may have impact on active Fe and Al which are he most active elements in soil P fixation.

In Table 5 – 9 listed are P adsorption capacities of 16 types of red soils in relation to active Fe and Al.

The equations for soil active Al (X) and soil P adsorption capacity (Y) are depicted as follows:

$$Y = 120.6 + 2.25\,X$$

$$r = 0.734^{**}$$

$$n = 16$$

The equations for soil active Fe (X) and soil P adsorption capacity (Y) are depicted as follows:

$$Y = 49.5 + 0.721\,X$$
$$r = 0.508^{**}$$
$$n = 16$$

Both equations indicate clearly that contents of Fe and Al are significantly, at 0.01 level, related to soil P adsorption capacity.

Table 5-9 Soil active Fe and Al and soil P adsorption capacity

Sample NO.	Location	Parent material	Landuse	Capacity (mg/kg · P)	Active Al (mg/100g)	Active Fe (mg/100g)
JX92-5	Suichuan	Red sandstone	Upland	87	125	162
7	Ninggang	Granite	Upland	198	120	64
10	Jinxian	Quaternary clay	Upland	382	164	153
18	Yujiang		Upland	770	183	104
22	Xunwu		Paddy	790	142	990
28	Taihe		Upland	107	58	130
ZJ92-9	Jinhua	Quaternary clay	Paddy	1002	177	56
11	Jinhua	Quaternary clay	Paddy	403	135	93
26	Juzhou	Quaternary clay	Upland	1161	259	312
29	Juzhou	Quaternary clay	Upland	1297	625	815
36	Juzhou	Quaternary clay	Upland	79	83	57
54	Lanxi	Quaternary clay	Upland	748	187	154
HN92-9	Hengyang	Quaternary clay	Upland	480	158	130
18	Changde	Quaternary clay	Upland	331	175	209
25	Shuangfeng	Limestone	Upland	215	152	165
28	Shuangfeng	Quaternary clay	Upland	476	192	453

5.3 Characteristics of Phosphate Rocks in China and Development of PAPR Fertilizers

The characteristics of the phosphate resources have been elaborated in Chapter 2. This part is devoted to discussing the need for developing PAPR with regard to the quality of the phosphate rocks in China.

5.3.1. Grade of the phosphate rocks in China

Although China has a huge reserve of phosphate rocks, they are in general quite low in grade, being 20.36% (P_2O_5) on average, thus arising a critical issue of how to make effective use of the medium- and low-grade phosphate rocks in China. So far, there are two ways being considered, direct application of phosphate rock powder and production of PAPR.

5.3.2. Reactivity of the phosphate rocks of China

Reactivity of phosphate rocks is a critical index for determining whether the phosphate rocks, especially medium- and low-grade phosphate rocks, can be used in direct application. Actually the topic of reactivity of phosphate rocks has been discussed in Chapter 2 already., it is only dealt here with the phosphate rocks properties that are related to effectiveness under direct application.

Effectiveness of phosphate rocks in direct application is closely related to how they are crystallized, and more precisely, to how their crystallization is associated with the isomorphous displacement of PO_4^{3-} with CO_3^{2-} in the lattice. The more they are replaced, the smaller the parameter a_0 of the lattice cell is. The so-called a_0 is the horizontal axis of a hexagonal prism of apatite. It is quite obvious that the more PO_4^{3-} are isomorphously replaced by CO_3^{2-}, the higher the ratio of CO_3^{2-}/PO_4^{3-} is and the smaller the a_0 is.

In the nature, francolite in sedimentary phosphate deposits has a_0 ranging between 0.9322 and 0.9376 nm, hydroxyfluorapatite between 0.9376 and 0.9421 nm or more.

Phosphate rocks with the highest a_0 value are in Kola Deposit of Russia and some others, being 0.938020 nm, while the rocks from Morocco maybe have the lowest a_0 value being 0.933090 nm. In Table 5 – 10 listed are a_0 values of some typical phosphate rocks (Hammond et al., 1986).

Table 5-10 Some typical phosphate rocks and their a_0 values

Region	Source of phosphate rocks	a_0 (nm)
Asia	El-Hassa of Jordan	0.9339
	Mussourie of India	0.9352
	Kaiyang of China	0.9372
Afirica	Gafsa of Tunisia	0.9328
	Hahotoe of Togo	0.9351
	Park W. of Niger	0.9365
Latin America	Bayovar of Peru	0.9337
	Pesca of Columbia	0.9346
	Patos de Miñas of Brasil	0.9370
USA	North Carolina	0.9322
	Middle Florida	0.9345
	Tennessee	0.9357

Table 5 – 10 shows that the phosphate rocks from Kaiyang of China, though, are one of the two types that have the highest a_0 value, and are regarded as the one with the highest effectiveness in direct application (Li

Chingkwei et al., 1992). Hence, it is quite obvious that the reactivity of the phosphate rocks of China is rather low. The study on crystalline properties of the phosphate rocks of China also revealed that their a_0 values ranged between 0.9353 nm and 0.9379 nm, and mostly around 0.9360 nm, which falls into the category of phosphate rocks of low reactivity.

Another laboratory index of reactivity of phosphate rocks is the amounts of P extracted with a variety of extractants. Generally there are three extractants being commonly used, i.e. neutral ammonium citrate (prevalent in the USA), 2% citric acid (in China and some other coutrnies) and formic acid (in Europe). In Table 5 – 11 listed are grading of amounts of P extracted with three different extractants and effectiveness in direct application (Hammond et al, 1986).

For comparison, in Table 5 – 12 listed are amounts of P extracted with 2% citric acid. It is clear that of the 8 major types of phosphate rocks, 4 or 50% are extremely low in effectiveness, 2 or 25% in the category of low and the most effective 2 or 25% still in the category of medium only.

The grading in Table 5 – 12 basically represents potential effectiveness of the major types of phosphate rocks of China in direct application. Although China has been working hard for several decades on direct application of phosphate rock powder (please refer to Chapter 4), so far there is not so much phosphate rock powder being really used in agricultural production. The reason is that most of the phosphate rocks of China is quite low in reactivity.

Since it is hard to make use of medium- and low grade phosphate rocks through direct application of phosphate rock powder, PAPR is a possible alternative.

Table 5-11 Grading of amounts of P extracted with three different extractants (%) and effectiveness in direct application

	Relative effectiveness			
	High	Medium	Low	Extremely low
Relative effectiveness (%)				
Mean	94	76	55	21
Range	85 ~ 99	74 ~ 79	42 ~ 67	12 ~ 28
Neutral ammonium citrate				
Mean	2.6	1.2	0.5	0.2
Range	2.4 ~ 2.9	0.8 ~ 1.5	0.2 ~ 0.8	0.1 ~ 0.3
2% citric acid				
Mean	5.8	2.9	2.5	1.3
Range	5.0 ~ 6.7	2.1 ~ 3.8	2.1 ~ 3.1	1.2 ~ 1.3
2% formic acid				
Mean	9.1	3.1	2.2	1.4
Range	7.6 ~ 10.4	2.2 ~ 3.6	1.0 ~ 3.0	1.4 ~ 1.5

Table 5-12 Amounts of P extracted with 2% citric acid from the major types of phosphate rocks in China and their grading

Origin	Type	% citric acid soluble P	Grade
Jinping, Jiangsu	Ancient cartogenic metamorphite	0.20	Extremely low
Jinxiang (Huji), Hubei	Sinian marine cartogene	0.72	Extremely low
Kaiyang, Guizhou	Sinian marine cartogene	2.90	Medium
Changde (Shimen) Hunan	Sinian marine cartogene	0.65	Extremely low
Jinning, Yunnan	Early Cambrian marine cartogene	2.74	Medium-low
Kunyang, Yunnan	Early Cambrian marine cartogene	3.23	Medium
Mianzhu (Qingping),	Cambrian marine cartogene	0.31	Extremely low
Shifang (Macaotan), Sichuan	Devonian marine cartogene	1.74	Low

5.4 Sulfur Resources and Production of sulfuric acid are both Insufficient for Production of Phosphate Fertilizers

China does not have much Sulfur resources, which exist mainly in pyrite and associated pyrite deposits. According to existing statistics (Jiang Shanxiang, ed. 1999), by the end of 1996, China had discovered pyrite deposits in 493 places all over the country, with a total reserve of 4630 million tons (ore), of which 1470 million tons is of industrial reserve and 3160 million tons of prospective reserve. Of the total reserve, the mean S content was around 17%, and only 170 million tons of ores were above 35% in S content. In China pyrite is distributed mainly in Sichuan (920 million tons), Anhui (560 million tons), Inner Mongolia (500 million tons), and Guangdong (450 million tons).

A total of 260 associated pyrite deposits have been discovered, with a total reserve of 330 million tons (S), distributed mainly in Jiangxi, Shaanxi, Gansu, Qinghai and Anhui Provinces.

In 1997, China produced17.27 million tons of pyrite and associated pyrite (25% S), 0.23 million tons of sulfur (retrieved mainly from petroleum and natural gas) and a certain quantity of other S products, totaling about 7.77 million tons (S), out of which China produced 19.91 million tons of sulfuric acid and 6.408 million tons of P fertilizers (P_2O_5). Calculation on the basis that the production of 1 ton of P_2O_5 consumes 1 ton of S (equal to 3 tons of H_2SO_4), China is short of 19.23 million tons of H_2SO_4. The import of 0.74 million tons sulfur each year was obviously still insufficient to make up the gap. Since the sulfuric acid supply for P fertilizer production is still inadequate, PAPR is a favorite choice, because it saves sulfuric acid. This is why PAPR is called sulfuric acid-saving P fertilizers. Proceeding from this point, PAPR matches the situation of China.

Chapter 6. Production Methods, Economic Analysis and Proposed Technical Criteria of PAPR*

6.1 Methods for Production of PAPR and experimental Production

6.1.1. Production methods

There are two ways in producing PAPR: direct and indirect ones.

a Direct method

It is similar to the traditional method for producing superphosphate or double superphosphate with the whole process consisting of three or four steps:

- ***Step One***

Mix phosphate rock powder (90% of the material can pass a 100-mesh sieve) with sulfuric acid for reaction. The quantity of sulfuric acid needed per unit of phosphate rock powder is calculated in light of the chemical composition of the rocks. Theoretically, the production of each mol of P_2O_5 consumes 2.33 mol of sulfuric acid. According to the following table, the consumption of sulfuric acid (100%) for decomposing 1 kg of phosphate rock powder can be worked out in light of the contents (%) of P_2O_5, Fe_2O_3, Al_2O_3 and CO_2 in the rocks.

Table 6-1 Consumption of sulfuric acid with regard to rock composition in P_2O_5, Fe_2O_3, Al_2O_3 and CO_2

Component in phosphate rocks	P_2O_5	Fe_2O_3	Al_2O_3	CO_2
Sulfuric acid consumption per unit component (kg)	1.61	0.61	0.96	2.23

For instance, the phosphate rocks from a certain

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[*] This chapter is contributed by Prof. Dai Yuanfa

deposit contain 32% P_2O_5, 1.0% Fe_2O_3, 1.0% Al_2O_3 and 2.5% CO_2. Then the consumption of sulfuric acid for making the phosphate rocks into SSP is figured out in the following way:

$0.32 \times 1.61 + 0.01 \times 0.61 + 0.01 \times 0.96 + 0.025 \times 2.23 = 0.59$ kg 100% H_2SO_4/kg phosphate rocks. The concentration of sulfuric acid for industrial use ranges between 77% and 98% and is usually diluted to 65% ~ 75% before getting into reaction with phosphate rock powder. The solution is cooled down to 70°C through a heat exchanger.

- ***Step Two***

The pulp formed from the reaction of acid with the phosphate rock powder flows into a formation chamber where it solidifies due to steady crystallization of monocalcium phosphate out of liquid state. The material stays in the chamber for 0.5 ~ 4.0 hours and is sliced into rags, which are then at 100°C and have some plasticity.

- ***Step Three***

The rags are sent into a slaking warehouse and stored in piles, where reaction continues. The reaction is usually termed slaking. The process will last 2 to 6 weeks depending on properties of the phosphate rocks and the conditions of the preceding steps. During this period, the reaction will go on till it is complete. With the decrease in free acid, moisture and undecomposed phosphate rocks, available P content increases.

As is requested, before shipment as finished product, superphosphate ought to be crushed into powder to pass a 6-mesh sift. In some superphosphate mills in China, however, this crushing is skipped over.

- ***Step Four***

If granular fertilizers are to be made, the steam-sheafing method is used either before or after the slaking process. It saves steam before slaking.

The production of P'APR with high acidulation degree (40%) may use this method. When PAPR of low acidulation degree is to be produced, the concentration of sulfuric acid ought to be lowered to a proper extent so as to ensure full mixture of acid and phosphate rock powder. And when P'APR of a much lower acidulation degree (10% ~ 20%) is to be made, machines like a drum-like or disc-like granulating machine can be used. Acid is sprayed directly onto phosphate rock powder when it is being churned in the drum or disc for granulating. The two processes of acidulation and granulation are combined into one. IFDC has designed a stainless steel disc-like granulating machine. At the lower left corner of the disc concentrated sulfuric acid is first sprayed and then water is injected onto the phosphate rock powder in the disc. The material that flows out at the outlet of the machine is semi-finished product, which needs slaking for a period of time before shipping out as finished product (Schultz, 1986).

b Indirect method

Mix phosphate rock powder with slaked or unslaked superphosphate or double superphosphate according to the specifications of a product for soluble P content. During the mixing process, free acid in the superphosphate or double superphosphate reacts with phosphate rock and calcium diphosphate with alkaline materials in the phosphate rock powder (limestone or dolomite) or highly active calcium phosphate to form monocalcium phosphate. As superphosphate or double superphosphate, slaked or unslaked, is somewhat moist and plastic, it is hard to get them fully mixed up. To make the reaction proceed smoothly, the mixture is pressed or peened to squeeze out liquid, which may further react with phosphate rock powder. Generally, horizontal twin-shaft mixers are used to complete the process. Cage-shaped crushers with a rapidly twirling element, horizontal or vertical chain grinders can also be used to complete the mixing process that involves pressing and peening.

c Flowchart of squeezing granulation

CIRAD combines PAPR with compound fertilizers in production through the following technological process of squeezing granulation (Fig. 6 – 1)

The technological process CIRAD has designed can be used to produce both powdered PAPR and PAPR-based granulated compound fertilizers added with supplements customers may require, using squeezing and pressing method or conventional method. Therefore, it is advisable to set up one or two, at the utmost, production lines using either method in light of demand of the market lest that too complicated a technological process should affect utilization rate of the production lines.

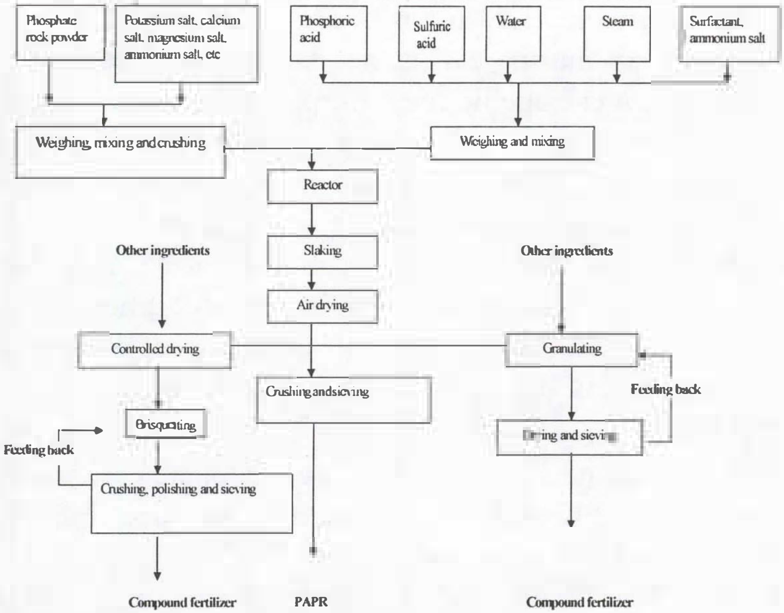

Fig. 6-1 : CIRAD's flowchart for PAPR production

6.1.2. Experimental production

In this paragraph an example of experimental production is elaborated. The Compound Fertilizer Research Institute of the Shanghai Academy of Chemical Industry tried to produce PAPR by following the technological process of the direct method (Liu Keming et al. 1990) without doing any detailed research on slaking and granulating processes. Following are results of the experiment, which may be used as a basis for economic analysis.

The experiment used phosphate rocks from the Jianshan Deposit and the Jiangchuan Deposit in Dianchi of Yunnan, the Kaiyang Deposit of Guizhou, the Yichang Deposit of Hubei and the Jinping Deposit of Jiangsu. Chemical compositions of the phosphate rocks from the five deposits are listed in Table 6–2. They are all marine cartogene. The Jinping Deposit of Jiangsu is a cartogenic metamorphous one, from which the phosphate rocks had undergone floating concentration. The phosphate rocks were extracted with neutral ammonium citrate solution and 2% citric acid. The amounts of P_2O_5 extracted varied, but were not high. In comparison with some soft phosphates, they belonged to the content category of moderate minus. This is believed to be related to their reaction reactivity.

The phosphate rocks of the five deposits are fairly good in quality and may be used to produce ordinary superphosphate with 16% ~ 18% of available P_2O_5. Since they have never been used to produce superphosphate, the author calculated, on the basis of his own experience, some major technical and economic indexes of the production (Table 6 – 3). Among the production costs, the cost of raw material accounts for 85%. If the unit price of the phosphate rocks is assumed to be at 5 ~ 5.5 yuan per unit P_2O_5, one ton of phosphate rocks containing 30% of P_2O_5 will cost 150 ~ 165 yuan/ton. The unit price of sulfuric acid is assumed to be at 320 ~ 380 yuan per ton. The production cost of per unit of P_2O_5 in the form of superphosphate will, therefore, be 12.42 ~ 13.81 or 14.34 ~ 15.68 yuan.

Table 6-2 Chemical composition of the phosphate rocks of the five deposits (%)

Item	Jianshan	Jiangchuan	Kaiyang	Yichang	Jinping
Total P_2O_5	31.48	29.04	30.24	32.29	37.10
Ammonium citrate soluble P_2O_5	4.46	3.15	2.61	3.17	1.08
2% citric acid soluble P_2O_5	6.52	6.33	5.37	6.05	3.43
CaO	41.95	38.47	44.17	45.19	51.67
Fe_2O_3	1.39	1.44	1.13	1.51	0.12
Al_2O_3	1.47	2.21	0.99	1.98	0.06
MgO	0.29	0.24	2.37	0.99	1.69
CO_2	2.48	1.25	5.38	2.88	4.35
SiO_2	17.29	22.96	9.67	8.95	0.15
F	3.17	2.60	2.70	2.56	3.22
Na_2O	0.88	0.06	0.28	0.43	0.02
K_2O	0.30	0.59	0.19	1.40	0.02
SO_3	0.14	0.21	0.56	0.87	0.25
P_2O_5 extraction rate (ammonium citrate)	14.17	10.85	8.63	9.82	2.89
P_2O_5 extraction rate (2% citric acid)	20.71	21.89	17.76	18.73	9.17

Table 6-3 Economic indexes of the production of superphosphate from phosphate rocks from the five deposits

Item	Jianshan	Jiangchuan	Kaiyang	Yichang	Jinping
Rock grade (P_2O_5 %)	31.48	29.40	30.24	32.29	37.40
Sulfuric acid consumption, kg H_2SO_4/1000kg rocks	585	525	623	612	704
Output rate, product/rocks	1.70	1.64	1.74	1.73	1.82
Consumption of raw material for producing each ton of superphosphate					
Sulfuric acid consumed kg/ton product	344	320	358	354	380
Rocks consumed kg/ton product	588	610	575	578	549
Cost of the raw materials used to produce each tone of the product *					
Sulfuric acid (320 yuan/ton)	110	102.4	114.56	113.28	121.6
Sulfuric acid (380 yuan/ton)	130.7	121.6	136.0	134.5	144.4
Rocks (5.0 yuan/ P_2O_5)	92.55	88.57	86.94	93.32	102.66
Rocks (5.5 yuan/	101.8	97.43	95.63	102.6	112.9

P_2O_5)					
Total (yuan) (sulfuric acid + rocks)	202.55	190.97	201.50	205.6	224.26
	232.5	219.0	231.6	237.0	257.3
P_2O_5 content in the product					
Total P_2O_5 (%)	19.07	17.70	17.37	18.66	20.55
Available P_2O_5 (%)	17.54	16.28	15.98	17.56	18.90
Total Cost to produce 1% of P_2O_5 in the final product (yuan)	12.42	12.68	13.65	13.81	13.64
	14.34	14.55	15.68	14.94	14.73
Raw material Cost to produce 1% of P_2O_5 (yuan) in raw material	10.50	10.73	11.60	11.07	10.91
	12.19	12.73	13.33	12.70	12.52

* Two prices are considered for both acid and rock

To partially acidulating phosphate rocks, sulfuric acid and phosphoric acid were used in the test, with emphasis on sulfuric acid. Three acidulation degrees were set as 30%, 50% and 70%. As crop response experiments showed that the product with acidulation degree at 50% fitted most to the acid soils in China, major parameters of the test of acidulating the phosphate rocks up to 50% in acidulation degree are listed in Table 6 – 4. In the product, the total P (P_2O_5) content ranged between 21.24% and 25.52%, about 3.25%, 3.54%, 5.12%, 4.22% and 5.02% higher respectively than in the corresponding superphosphate products. Its soluble P content was 7.37% ~ 11.13%, which showed that its P water-solubility ranged between 32.77% and 44.68%. Only 0.10% ~ 1.04% of P_2O_5 was soluble in neutral ammonium citrate solution and 1.02% ~ 4.10% in 2% citric acid solution. Based on P_2O_5 extraction in 2% citric acid, the available P content of the product was around 11.22% ~ 13.30% and its P_2O_5 availability 47.60% ~ 62.61%.

Table 6-4 Major technical parameters of PAPR (50% in acidulation degree) from the rocks of the five deposits

Item	Jianshan	Jiangchuan	Kaiyang	Yichang	Jinping
Rock Grade (% P_2O_5)	31.48	29.04	30.24	32.29	37.40
Total P in product (%)	22.32	21.24	22.49	22.87	25.52
Water Soluble P(%)	8.41	9.49	7.37	8.52	11.13
P water-solubility (%)	37.67	44.68	32.77	37.25	43.61
P soluble in neutral ammonium citrate%	0.78	0.56	1.04	0.86	0.10
Total P extracted in ammonium citrate* %	9.19	10.05	8.41	0.38	11.23
Extraction rate %	41.17	47.31	37.39	41.01	44.00
P soluble in 2% citric acid %	3.73	3.87	3.85	4.10	1.02
Total P extracted in 2% citric acid % *	12.14	13.36	11.22	12.62	12.15
Extraction rate %	54.61	62.61	49.88	55.18	47.60
Free acid P_2O_5%	5.56	6.70	2.87	6.47	5.11
Free water %	9.70	9.00	9.89	7.97	8.20

Note: Since in the experiment the products' maturing processes were not determined as was required, the data obtained on free acid, soluble P, citric acid soluble P and total P are not those of the finished products. There are some deviations, which are, however, believed not being too large.

*: Water soluble P is included.

The data in the table show that discrepancies exist in some technical parameters between PAPR and some of the discrepancies are quite big, which is attributed to differences in characteristics, mainly in two aspects, between rocks. One is chemical composition and the other reaction reactivity. Chemical compositions of the phosphate rocks from the five deposits are already listed in Table 6 – 2, showing that the grade of the rock is positively related to total P_2O_5 and available P_2O_5 contents in its product, while content of carbonate (expressed in CO_2 in Table 6 – 2) of the rock negatively to quality of its product. Reaction reactivity of the rocks may have great influence on production of superphosphate, double superphosphate and PAPR. The higher the reaction reactivity, the shorter the maturing period is and the quicker the production process. In this experiment, rocks from Jinping of Jiangsu, though high in content, were deeply metamorphosed phosphate. So they were quite low in reaction reactivity and in addition, high in CO_2 content. The PAPR product out of the rocks was then low in some technical indexes.

The consumption and cost of raw materials, production cost per unit P_2O_5 and some other technical and economic indexes of the production of PAPR (50% in acidulation degree) out of rocks from the five deposits are listed in Table 6 – 5.

Table 6-5 Technical and economic indexes of PAPR produced out of rocks from the five deposits

Item	Jianshan	Jiangchuan	Kaiyang	Yichang	Jinping
Content (P_2O_5 %)	31.5	29.40	30.24	32.29	37.40
Sulfuric acid consumption, kg H_2SO_4/1000kg rocks	292	263	312	306	354
Output rate, product/rocks	1.4	1.36	1.34	1.41	1.47
Consumption of raw material for producing each ton of PAPR					
Sulfuric acid consumed kg/ton product	206.4	193.38	232.83	217.02	240.82
Rocks consumed kg/ton product	709.2	735.29	746.26	709.22	680.27
Cost of the raw materials used to produce each tone of the product					
Sulfuric acid (320 yuan/ton)	66.00	61.76	74.49	69.44	77.05
Sulfuric acid (380 yuan/ton)	78.42	73.48	88.47	82.46	95.51
Rocks (5.0 yuan/ P_2O_5)	111.59	105.72	112.79	114.46	127.16
Rocks (5.5 yuan/ P_2O_5)	122.79	117.44	124.11	125.95	139.43
Total (yuan) (sulfuric acid + rocks)	177.59	168.48	187.28	183.90	204.21
	201.20	190.92	212.58	208.41	235.40
Total	22.32	21.24	22.49	22.87	25.52
Cost of raw materials/P_2O_5 (yuan)	7.96	7.93	8.35	8.04	8.00
	9.01	8.98	9.45	9.11	9.22
Production cost/P_2O_5 (yuan)	9.36	9.34	9.82	9.46	9.44
	10.60	10.56	11.11	10.71	10.85

6.2 Economic analysis

In this section comparison is made in raw material cost and production cost per unit of P_2O_5 between PAPR (50% in acidulation degree) and superphosphate (SP) out of rocks from the five deposits. Total P_2O_5 rather than available P_2O_5 in the products was used as the basis for the comparison, to which are referred results of crop response experiments. In Table 6 – 6 listed are major technical and economic data for comparison. Results of the comparison go as follows:

Total P_2O_5 contents in superphosphate ranged between 17.37% and 20.55%, and averaged 18.57%, whereas in PAPR between 21.24% and 25.52%, and 22.88%, showing that the latter had 4.31% more P_2O_5 and 23.3% higher in relative value.

The content of available P_2O_5 in superphosphate varied from 15.98% to 18.90%, being 17.25% on average while in PAPR it did from 11.22% to 13.36%, being 12.30% on average. The comparison shows that the latter had only 71.3% as much as the former did.

As regard to consumption of raw materials, it consumes 320 ~ 380 kg or 351 kg on average H_2SO_4 (100%) to produce each ton of superphosphate, while it needs only 193.4 ~ 240.8 kg or 218.1 kg on average to produce one ton of PAPR. Obviously the latter uses 133.1 kg or 38% less H_2SO_4. And the production of one ton of superphosphate takes 575 ~ 610 kg or 580 kg on average phosphate rocks whereas the production of one ton of PAPR requires 680 ~ 746 kg or 715.9 kg on average. The latter consumes 136.9 kg or 24.36% more.

The cost of raw materials is estimated on the basis that the price of one ton H_2SO_4 (100%) is 320 yuan and that the price of per unit of P_2O_5 is 5.0 yuan. In this way, the cost of raw materials for each ton averages 205.17 yuan and 179.39 yuan respectively for superphosphate and PAPR. It is clearly shown that the cost of the latter is 25.78 yuan or 12% lower.

Production cost is often counted as 115% of the cost of the raw materials. For each ton of superphosphate it is, therefore, 224.67 yuan and 242 yuan on average. For each ton of PAPR it is 211.04, being 31 yuan less.

The calculation of the production cost of per unit P_2O_5 is done by dividing the production cost of the product with the total P_2O_5 content in the product. In this case the cost of per unit P_2O_5 is 13.03 yuan with superphosphate, and 9.46 yuan with PAPR. The cost with the latter is 72.6% of that of the former. This result is obtained on the basis that superphosphate and PAPR equivalent in total P_2O_5 content are the same in effectiveness. If the latter is lower in effectiveness than the former, its relative cost of per unit P_2O_5 is calculated on the basis of its relative effectiveness with that of the former as 100 (Table 6 – 7).

Table 6-6 **Comparison between superphosphate and PAPR in technical and economic data**

Item	Jianshan	Jiangchuan	Kaiyang	Yichang	Jinping	Mean
Total P_2O_5 (%) in product						
Superphosphate	19.07	17.70	17.37	18.66	20.55	18.57
PAPR	22.32	21.24	22.49	22.87	25.52	22.88
% PAPR/SP	117.0	119.8	129.5	122.6	124.2	123.3
Available P_2O_5 (%) in product						
Superphosphate	17.54	16.28	15.98	17.56	18.90	17.25
PAPR	12.14	13.36	11.22	12.62	12.15	12.30
% PAPR/SP	69.2	92.1	70.2	71.5	69.3	71.3
Consumption of raw materials Sulfuric acid (kg/ton product)						
Superphosphate	344	320	358	354	380	351.2
PAPR	206.4	193.4	232.8	217	240.8	218.1
% PAPR/SP	60.0	60.0	65.0	61.3	63.4	62.0
Phosphate rocks (kg/ton product)						
Superphosphate	588	610	575	578	549	580
PAPR	709.2	735.3	746	709	680	715.9
% PAPR/SP	120.6	120.5	129.7	122.7	123.8	123.4
Cost of raw materials * Sulfuric acid (yuan/ton product)*						
Superphosphate	110.0	102.4	114.6	113.3	121.6	112.4
PAPR	66.0	61.8	74.5	6934	77.1	69.8
% PAPR/SP	60.0	60.4	65.0	61.3	63.4	62.0
Phosphate rocks (yuan/ton product)*						
Superphosphate	92.55	88.57	86.94	93.32	102.66	92.79
PAPR	111.59	106.72	112.79	114.46	127.16	114.55
% PAPR/SP	120.5	120.5	129.7	122.6	123.8	126.46
Subtotal of the cost of raw materials (yuan/ton product)*						
Superphosphate	202.55	190.97	201.5	206.6	224.25	205.17
PAPR	177.59	168.48	187.28	183.9	204.26	179.39
% PAPR/SP	87.67	88.22	92.90	89.0	91.18	87.43
Production cost (yuan/ton product)*						
Superphosphate	238.29	224.67	237.05	243.05	263.82	242.0
PAPR	208.92	198.21	220.33	216.35	240.30	211.04
% PAPR/SP	87.67	88.22	92.94	89.01	91.08	87.20
Production cost of per unit of P_2O_5 (yuan)*						
Superphosphate	12.49	12.69	13.64	13.02	12.83	13.03
PAPR	9.36	9.33	9.79	9.45	9.41	9.46
PAPR/SP	74.9	73.5	71.8	72.5	73.3	72.6

*: Calculations are done based on two different prices of sulfuric acid and phosphate rocks.

Table 6-7 Indexes of Relative effectiveness and relative cost of PAPR as compared to Superphosphate

Relative effectiveness	Relative cost
100	71.7
98	73.2
95	75.5
93	77.1
90	79.7

Note : relative cost increases as the effectiveness decreases in the same proportion

Conclusion from economic comparison between superphosphate and PAPR depend mainly on two factors: 1) Cost comparison between the two. On the basis of per ton of product, PAPR consumes less sulfuric acid but more phosphate rocks than superphosphate. In the US and some other countries, the unit price of sulfuric acid is very close to that of phosphate rocks (30% ~ 23% P_2O_5), but in China, it is much higher. Especially in regions quite close to phosphate deposits, the cost of transporting phosphate rocks is low, making it much more economical to produce PAPR. When calculation is made on the basis of total P_2O_5, the production of PAPR is always economical. 2) Effectiveness of unit P_2O_5 on the basis of total P. The conclusion of the above discussion is that when the effectiveness of PAPR (50% in acidulation degree) is equal to 72% ~ 80% that of superphosphate, the economic benefits of the two are the same. But in this chapter, the effectiveness of the PAPR used in the test is 95% ~ 98% that of superphosphate. So production and consumption of PAPR costs 22% ~ 25% less than of superphosphate.

6.3 Technical criteria for PAPR

There are concerns that extension of PAPR will induce false and inferior P fertilizers to swarm into the market, thus damaging farmers' interest. The concerns are, though, understandable. Market economy is nevertheless a system that is regulated by laws. It is, therefore, essential to work out criteria for the product of PAPR and for its test analysis as well. In this chapter, basic contents of the criteria (50% in acidulation degree and sulfuric acid as acidulating agent) are proposed for further discussion and reference (Table 6-8).

It is pivotal to set total P_2O_5 content as the major technical index. Besides it is still necessary to specify contents of soluble P_2O_5 and 2% citric-acid-extractable P_2O_5. The two portions of P_2O_5 consist of readily available P., while the P_2O_5 in the undecomposed phosphate rocks is slowly available P.

With phosphate rocks of 28% ~ 32% P_2O_5 as raw material, the product (50% in acidulation degree) will contain 19% ~ 23% total P_2O_5. It is required that the content of soluble P_2O_5 should not be less than 33% of the total P and readily available P_2O_5 not less than 50%. Hence, here are major technical criteria for PAPR:

Table 6-8 Proposal for PAPR technical criteria

Product grade	Grade I	Grade II	Grade III	Grade IV
Total P_2O_5 %$\geqslant$	25	23	21	19
Water Soluble P_2O_5 % $\geqslant$	8.0	7.5	6.5	6.0
Available P_2O_5 % $\geqslant$	14.5	11.5	10.5	9.5

The criteria of free acid and free water for PAPR ought to be the same as or just a bit lower than that for superphosphate, respectively.

The same analyzing methods and criteria ought to be used for PAPR and superphosphate to determine total P, soluble P, free acid and moisture. For determination of citric acid soluble P, 2% citric acid solution is used with reference to the standard analyzing method for Calcium-Magnesium Phosphate.

Its physical properties and package requirements are the same as superphosphate's. It is encouraged to prepare PAPR low in acidulation degree into granules.

And when necessary, for instance for strongly P fixing soils, PAPR high in acidulation degree can be prepared into granules, better into fine granules (0.5 ~ 1.3 mm).

6.4 Effects of characteristics of phosphate rock on technology and economy of PAPR production

Some people hold that the production of PAPR does not require as much quality of phosphate rocks and may use some phosphate rocks that are hard to use for fully acidulated P fertilizer. It is true under certain conditions, but can not be overstressed. From the above discussion it is already known that quality of phosphate rocks has impact on PAPR technologically and economically as much as on superphosphate. For example, carbonate-based impurities (limestone and dolomite) in phosphate rocks affect sulfuric acid consumption. The increment of each 1% in CO_2 content of phosphate rocks will increase sulfuric acid consumption by 22.3kg/100kg rocks regardless of acidulation degree. Table 6 – 4 shows that with the phosphate rocks from Kaiyang of Guizhou containing 5.38% CO_2 (Table 6 – 1), the production of each ton of PAPR (50% in acidulation degree) requires 746.26 kg of the rocks and 232.83 kg of sulfuric acid, of which about 89.5 kg or 38.4% is used to decompose carbonate minerals. Consequently, when phosphate rocks high in carbonate content are to be produced into PAPR with soluble P_2O_5 no less than 33%, its acidulation degree should be kept beyond 50%. For PAPR production, theoretical sulfuric acid consumption can be reckoned according to the following equation:

$$A = X[1.61a + 0.61b + 0.96c] + 2.23d$$

where *A* stands for sulfuric acid consumption (kg) per 10 kg phosphate rocks;

X for acidulation degree with that of superphosphate being 1.0;

a for P_2O_5 content in the phosphate rocks (%);

b for Fe_2O_3 content in the phosphate rocks (%);

c for Al_2O_3 content in the phosphate rocks (%);

d for CO_2 content in the phosphate rocks (%)

As carbonate minerals in the rocks are always first to be decomposed, it is necessary to calculate the portion of sulfuric acid consumed to decompose carbonate minerals on the basis of 100% of their stoichiometric amount when sulfuric acid consumption in the production of PAPR of any acidulation degree is to be reckoned.

6.5 Discussion

It is technologically mature and feasible to remold some of the existing superphosphate plants into PAPR producers. The product, designed for acid soils, will find a certain place in the market.

Based on the results of the research work in China it is held that for most phosphate deposits and acid soils in China, 50% acidulated PAPR is quite reasonable, because the results of crop response experiments show that the effectiveness of this kind of PAPR equals to 95% ~ 100% that of superphosphate on the basis of equivalent total P.

Comparison between PAPR (50% in acidulation degree) and superphosphate in economy depends on specific value of the unit prices of sulfuric acid and phosphate rocks. On the basis of the assumed unit prices of sulfuric acid and phosphate rocks in this chapter, the production cost of PAPR (50% in acidulation degree), based on total P_2O_5, is 25% ~ 30% lower than that of superphosphate. As the prices of sulfuric acid and phosphate rocks that superphosphate plants can get vary from region to region in China, the comparison can only be used for reference. In the world market, the production cost of 98% sulfuric acid is roughly equal to the market price of phosphate rocks containing 31 ~ 32% P_2O_5, while in most plants in China, it is much higher than the price of phosphate rocks delivered at the plant. Therefore, in China it is especially economical to produce sulfuric acid-saving PAPR fertilizers for the sake of saving sulfuric acid as long as its effectiveness is equivalent to all-soluble P fertilizers in acid soils.

In this chapter, technical criteria for PAPR products are put forward. Products are divided into several grades in light of their contents of total P, soluble P and citric-acid-soluble P. For their standards for free acid and free water, please refer to those for superphosphate. The quality of raw material phosphate is also discussed and an equation for computing theoretical acid consumption is proposed for reference.

Chapter 7. Researches on PAPR in Other Countries: A Review

Since PAPR has its own advantages and prospect in application, quite a number of countries have been conducting researches in this aspect. Among them are the USA, Germany, countries in East and West Europe, India, Israel, New Zealand, and countries in Africa and Latin America. Some papers have been published reviewing crop responses of wheat, barley, oat, rye, corn, sorghum, rice, potato, forage grasses, etc. to PAPR (Hagin, 1985; Hammond et al., 1986; Stephen et al., 1986; Chien et al., 1988; Bolan et al., 1990; Golden et al.; Rajan et al., 1993). Following is a brief summary of the development of the related researches.

7.1 Early researches

As early as in 1930, Finland already began industrial production of PAPR (Schultz, 1986), but the earliest research report on PAPR probably appeared in 1957 (cited from Rajan, 1993). The paper, whose author was Nordengren, was published in a journal named "Fertilizer and feeding stuffs J.". It was said in the reported that PAPR, termed Kotka then, had been used in Finland for almost 30 years. After the 1960s, Germany and France started their production of Kotka, generally using H_2SO_4 to acidulate phosphate rocks. With an acidulation degree of 50%, the fertilizer showed high effectiveness, about 90% that of superphosphate in acid peat soils ($pH < 5.2$), but only 80% in acid peat soils with higher pH ($pH > 5.2$). So, the effectiveness of this kind of PAPR fertilizer was more or less equal to that of superphosphate in test soils. Marwaha (1983, cited from Stephen, 1981) reported that in 1961 experiments of using H_3PO_4 or HNO_3 to acidulate phosphate rocks with high carbonate resulted in PAPR equal in effectiveness to superphosphate (pot experiment). Beginning from 1964, Mclean, et al. carried out a series of researches (Mclean et al., 1964), revealing that PAPR of phosphate rocks from Florida acidulated with H_3PO_4 at 10% or 20% had the same effectiveness as that of superphosphate, a completely acidulated fertilizer, in acid soils.

Later, other scientists confirmed again that the effectiveness of PAPR of varied acidulation degree could be equivalent to that of TSP.

7.2 Researches at the International Fertilizer Development Center (IFDC)

In late 1970s and 1980s, IFDC carried out a huge number of field experiments in Latin America, Asia and Sub-Sahara of Africa, studying effect of acidulation on effectiveness of PAPR in different soils and under different crops. It reached a general conclusion that the effectiveness of PAPR of phosphate rocks acidulated to around 50% with H_2SO_4 or to about 20% with H_3PO_4 was quite similar to that of TSP or superphosphate in some soils and under certain crops.

In over 60 large-scaled field experiments with a variety of soils and crops, the effectiveness of PAPR was the same as that of TSP (Chien et al., 1989, cited from Pelovski, 1995).

In Africa, the effectiveness of PAPR made out of non-active phosphate rocks was much higher than that of direct application of phosphate rocks and approximate to that of superphosphate (cited from Pelovski, 1995).

Based on the experiments in Asia, Hammond (1986) came to believe that PAPR with acidulation degree up to 50% could have the same effectiveness as totally acidulated P fertilizers.

The experiments in India showed that even if on soils low in P fixation, PAPR was close to TSP in effectiveness (Chien et al., 1988).

7.3 Experiments in Germany and East European countries

Hagin (1985) summed up the experiments in Germany and some East European countries as listed in Tables 7 – 1 and 7 – 2.

Table 7-1 Experiments on crop response to PAPR in Germany (1961 ~ 1981)

Soil pH	Total number of trials	Number of trials		
		PAPR = SSP*	> SSP	< SSP
4.6 ~6.5	57	46	4	7
6.6 ~ 7.5	45	4	3	0

*: SSP = superphosphate

Table 7-2 Relative effectiveness of PAPR (NK + TSP = 100%)

Treatment	Bulgaria (wheat)	Czech (potato)	Poland (wheat)	Former USSR	
				Wheat	Potato
NK	90	40	90	64	81
NK + PAPR	100	109	104	102	109

Some experiments in some East European countries demonstrated that the effectiveness of PAPR was at the same level as that of TSP.

Table 7 – 1 clearly shows that in soils with pH ranging between 4.6 and 6.5, nearly 90% of the trials demonstrated that the effectiveness of PAPR was equal or greater than that of superphosphate while in soils with pH ranging between 6.6 and 7.5 it reached 100%.

The experiments in Bulgaria, Czech, Poland and former USSR also indicated that PAPR had good crop response ((Please refer to Hagin, 1985).

7.4 Experiments in New Zealand

Years of large-scaled field experiments (Rajan et al., 1994) showed that in soils with pH ranging between 5.5 and 6.3 and P fixation capacity between 25% ~ 97%, PAPR enjoyed significant crop response from forage grasses. Results also revealed that PAPR using H_2SO_4 as acidulating agent was inferior to PAPR using H_3PO_4 in crop response, though their water soluble P contents were the same. It is believed that when H_2SO_4 is used to acidulate phosphate rocks, $CaSO_4$ coating is formed around unacidulated rocks, thus affecting their solubility.

The experiments in New Zealand also indicated that PAPR using H_2SO_4 as acidulating agent with acidulation degree up to 30% and soluble P accounting for 50% of total P showed effectiveness similar to that of TSP (cited from Pelovski et al., 1995). Some results also showed that PAPR with soluble P accounting for 30% ~ 40% of total P was also similar to TSP in crop response. In short, results of quite a number of experiments demonstrated that on the basis of unit P entering soil solution, PAPR is better than TSP, especially when it is used continuously.

Rajan (1982) used H_3PO_4 to acidulate phosphate rocks from North Carolina and prepared them into granules 0.1 ~ 0.3 mm in size. They were the same as TSP in crop response from ryegrass (pot experiment) in the first 12 months and surpassed TSP in the follow-up 6 months.

7.5 Experiments in Israel

In 1985, Hagin summed up the experiments in Israel. Their interest was focused on calcareous soils (pH 6.9 ~ 7.8, lime content 2% ~ 35%, sandy loam to clay). Fertilizers they used in the experiments were mixture of TSP and phosphate rock powder (Arad phosphate, a kind of active phosphate in Israel) of varied ratio and sometimes PAPR out of Arad phosphate rocks was also used. The properties of these fertilizers are listed in Table 7 – 3. Results of the pot experiments were shown as in Table 7 – 4.

Table 7-3 Properties of the fertilizers used in the experiments in Israel

Code	Composition of fertilizers	% Water Soluble P
TSP	TSP	92.8
TSP – A33	2/3 TSP + 1/3 phosphate rock powder	67.0
TSP – A50	1/2 TSP + 1/2 phosphate rock powder	50.0
TSP – A66	1/3 TSP + 2/3 phosphate rock powder	32.5
TSP – A48*	1/2 TSP + 1/2 phosphate rock powder	52.0
PAPR – 40	Acidulated with H_3PO_4	50.3

*: All the fertilizers were used in pot experiments, except TSP – A48, which was used in field experiments.

Table 7-4 Results of the experiments in Israel (crop response to TSP = 100%)

Soil	TSP (93)	TSP–A33 (67)	TSP–A50 (50)	TSP–A66 (33)	PAPR–40 (50)*
1. Clay, pH 7.6, lime content 35%					
	100	90	101	–	91
2. Sandy clay, pH 7.8, lime content 23%					
	100	98	94	82	91
3. Sandy loam, pH 6.9, lime content 2%					
	100	96	95	92	97

*: The data in parentheses are % water soluble P

From Table 7 – 4, it is clearly shown that when soil pH is over 7, it is better for PAPR to have soluble P beyond 50% in total P, otherwise crop response of the

PAPR would be lower than that of fertilizers of soluble P. But when soil pH is below 7, relative crop response is higher to all fertilizers. In any case, fertilizers with soluble P content over 50% are better and their effectiveness is approximate to TSP's.

The experiments in both Germany and Israel showed that PAPR might be used effectively in calcareous soils (Hagin, 1985). Just as was mentioned above, in this case, it is better to prepare PAPR with soluble P content over 50% or with total acidulation degree beyond 50%.

7.6 Effectiveness of mixture of soluble phosphate fertilizer and phosphate rock powder

The mixture of soluble P fertilizer with a certain amount of phosphate rock powder is also generally called partially acidulated P fertilizer, because its main components are just the same as PAPR's and so it can be inferred that its effectiveness is close to PAPR's, too. As a matter of fact, the first PAPR, or Kotka, used in Finland was also a mixture of the same nature.

Scientists in Israel once used the *X*–ray diffraction method to determine a mixture of TSP plus phosphate rock powder (RP) and PAPR acidulated with H_3PO_4 to 40%, discovering that the two were basically the same in chemical composition, soluble P form, citric-acid-soluble P form, etc. (Hagin et al., 1985). Field experiments with corn also indicated that the mixture of TSP + RP and TSP was more or less the same in crop response and crop P uptake, which is proof that TSP + RP and PAPR had the same effect.

IFDC (Chien, 1989) has also conducted similar tests. On acid soils (pH 4.8 originally and raised up to 6.5 by liming), large-scaled field experiments were carried out on corn response to application of a mixture of highly active phosphate rock powder and TSP, with results showing that it was the same as to TSP when its RP proportion remained under 50%. It can, therefore, be concluded that the mixture of soluble P fertilizer with phosphate rock powder may have basically the same effectiveness as PAPR of the same acidulation degree.

7.7 Conclusions of some researches conducted in other countries

Generally speaking, the effectiveness of PAPR, especially on neutral soils, will not be so high as that of soluble P fertilizers unless it uses highly active phosphate rocks as its raw material and its acidulation degree is over 50% (Terman et al., 1967; Lutz, 1973). Singh (1976) acidulated phosphate rocks with HNO_3 to 30%, 50% and 70%, separately. Of the three PAPRs, the first two were lower than superphosphate in effectiveness. Hammond et al. (1980) conducted pot experiments, which also showed that PAPRs with acidulation degree of 20%, 30% and 40% were all lower than TSP in effectiveness. The one with acidulation degree of 20% was only 53% ~ 76% as effective as TSP.

Of course, with conditions varying, what a proper acidulation degree should be depends on a series of factors, such as soil, crop, phosphate rocks, etc..

PAPR has some residual effect, particularly in acid soils. When a PAPR experiment lasts longer, the relative effectiveness of PAPR is higher. For example, Hammand et al, (1980) found that PAPR acidulated to 20% with H_3PO_4 was 53% ~ 76% as effective as TSP on the first cropping and 79% ~ 90% on the third cropping.

Rajan (Stephen, 1993) had a two-year experiment, which indicated that the residual effect of PAPR (H_3PO_4) of 20%, 30% and 50% in acidulation degree was equal to 97% ~ 108% the effectiveness of TSP.

Davies (1984) carried out experiments on pasture. The result was that granulated PAPR (50% soluble P, acidulated with H_3PO_4) was equal to 60% ~ 70% of superphosphate in crop response in the first year and 89% ~ 115% in the second year, showing significant residual effect.

Researches also reveal that PAPR can also be prepared by blending phosphate rock powder direct with soluble P fertilizer. They can be simply blended together or granulated after blending, or phosphate rock powder is added in during the last stage of the production process of superphosphate (Bolan et al., 1987; Chien et al., 1987; Memom et al., 1990). The three types of products are almost the same in effectiveness. The last method has been used in New Zealand.

Chien et al. (1987) blended TSP with low active phosphate rock powder. The mixture was the same in effectiveness as PAPR acidulated with H_3PO_4 (the mixture and the PAPR were also the same in soluble P content, size of granules and total P content). It is believed that when phosphate rocks contain much Fe and Al, blending is a better method to produce PAPR, because it may reduce soluble P fixation by Fe and Al as compared with the acidulation method. In this way, phosphate rocks low in quality may be used.

Adding phosphate rock powder at a ratio of 3:7

(RP:SSP) during the last stage of the production process of superphosphate when it is still wet produces product that is found to be slightly lower than SSP in effectiveness.

The economic and social benefits of producing PAPR should be affirmed. It does not need much investment to remold a superphosphate plant into a PAPR plant. Many countries in the world including some West European countries have already established such an industry. But China has not yet had a real PAPR industry. It is, however, believed that this type of fertilizer has a brilliant future.

What should be the acid to be used in producing PAPR depends on the following factors:

- Availability of the acid to be retained
- The targeted P content of the final product. For instance, PAPR acidulated with H_2SO_4 to 50% in acidulation degree contains less P_2O_5 than the raw phosphate rocks do, while PAPR with H_3PO_4 to 30% contains more P_2O_5 than the raw phosphate rocks do.
- Properties of phosphate rocks (see infra).
- Soil S status. In regions with soils deficient in S, it is better to use H_2SO_4 as acidulating agent.

This chapter has already dealt with the effect of raw phosphate rocks. As to what type of phosphate rocks should be used to produce PAPR, there are two factors influencing the decision.

- One is the concern of how to make full use of phosphate rock resources. For instance, in China, most of the phosphate deposits are moderate or low in grade, and some even not fit for direct use in the production of soluble P fertilizers. In this case, how to make full use of the resources has become the first priority for consideration. Nevertheless, quality of products is also an important consideration. If phosphate rocks moderate or low in grade are used to produce PAPR, the production consumes more acid (on the basis of acid consumption of per unit soluble P) and the products are low in available P content and effectiveness, which goes against the objective of the production of PAPR. The production of PAPR must be based not only on saving of sulfuric acid but also fair effectiveness of the product. So careful consideration should be made to balance the two factors as to making full use of the resources as well as producing quality fertilizers.

o The other one is that leaving aside the issue of grade, phosphate rocks high in reactivity are to be used. They consume less acid in producing PAPR of the same effectiveness because they need lower acidulation degree. When acidulated with H_2SO_4, high quality phosphate rocks generate less $CaSO_4$ coating because phosphate rocks high in reactivity have a large specific surface ($30 \sim 50$ m^2/g), about 10 times that phosphate rocks low in reactivity do.

What types of soils are fit for application of PAPR? PAPR is applicable to a broad range of soils. However, it is generally more effective on soils with $pH < 7$. On soils different in pH, it is better for PAPR to have different% of water soluble p, which can vary roughly within such a range:

- On strong acid soils, the optimal water soluble P of PAPR should vary between 20% and 40% of its total p.
- On weak acid soils, between 50% and 60%, and
- On calcareous soils between 60% and 80% (because they need more acid).
- It is also held that soil P fixation capacity (adsorption capacity) also influences determination of optimal acidulation degree of PAPR. For instance, with pH around 5, soils high in P fixation capcity favor PAPR of 20% ~ 30% in acidulation degree, but soils low in P fixation capacity are fit for PAPR of 30% ~ 40%.
    - With pH at 6, soils high in P fixation capacity favor PAPR of 40% ~ 50% in acidulation degree, but soils low in P fixation capacity are fit for PAPR of 50% ~ 60%.
    - With pH at 7, soils high in P fixation capacity favor PAPR of 60% ~ 70% in acidulation degree, but soils low in P fixation capacity are fit for PAPR of 70% ~ 80%.
    - Although the above comment can only be regarded as a general conception of nature, it may, in principle, be used as a reference.

Chapter 8. ISSAS' Study on PAPR in the 1970s

As early as in the 1960s, the Sichuan Province Academy of Agricultural Sciences initiated a research project on PAPR and then was followed by the Institute of Soil Science, Academia Sinica (ISSAS), Shanghai Academy of Chemical Industry, etc. in this field. Here in this book, emphasis is put on the work done by ISSAS.

During the period of 1973 ~ 1977, ISSAS started its research on PAPR. Years of researches on direct application of phosphate rock powder revealed that most of the phosphate deposits were too low in reactivity to be used directly. So the basic objective of the institute in unfolding the research was to explore whether it was feasible or not to make use of the phosphate deposits low in reactivity through partial acidulation. Consequently, the phosphate deposit in Jinping of Jiangsu, one of the deposits with the lowest reactivity, was chosen as the object of the research. The Jinping deposit is of deeply metamorphosed phosphate deposited in the Presinian. Its rocks are of the structure of crystalloblast and scaly crystalloblast and its phosphate mineral is apatite, whose typical chemical composition is 13.45% of P_2O_5, 36.58% of CaO, 9.92% of MgO, 23.76% of CO_2, 10% of Fe_2O_3, 0.68% of Al_2O_3, 1.32% of F and 0.199% of lattice CO_2, from which it is known that isomorphous replacement is very low there. This type of deposit is regarded as one of those lowest in reactivity in China and unfit for direct application. Another deposit chosen for the experiment was the one in Kunyang of Yunnan. It is also a deposit moderate-minus in reactivity and the most important sedimentary phosphate deposit of China. Its phosphate mineral is kind of low-micro carbonate fluorapatite, whose typical chemical composition is 28.16% of P_2O_5, 39.08% of CaO, 1.31% of MgO, 4.83% of CO_2, 1.59% of Fe_2O_3, 2.22% of Al_2O_3, 15.02% SiO_2, 2.65% of F and 1.5% of lattice CO_2. In fact, it belongs to the category of low carbonate apatite.

The designed experiment was two-fold, field experiment and pot experiment. For field experiment, a total of 23 test fields were set up in Yixing, Huaiying, Jiangdu, Tongshan, Xiangshui, Guangyun and Xuyi of Jiangsu. Crops used in the experiment included sweet potato, rapeseed, milkvetch, common vetch, Sesbabia, soybean, pea, rice and wheat. The acreage of each plot was 66m^2 and each treatment had three replicates. The pot experiment was carried out in Nanjing.

The PAPR (H_2SO_4, 50% in acidulation degree) used in the field experiment was prepared by the Xuzhou Phosphate Fertilizer Plant at the request of ISSAS (Table 8 – 1 for properties of the fertilizer) and PAPRs varied in acidulation degree for the pot experiment were prepared by the institute itself (acidulated with H_3PO_4 and H_2SO_4).

Table 8-1 Properties of P fertilizers used in the field experiment

Item	SSP (100% acidulation)	PAPR (50% acidulation)
Total P (P_2O_5 %)	15.27	18.55
Citric acid soluble P (P_2O_5 %)	14.07	9.30
Free acid (%)	9.68	0.88
P transformation rate (%)	92.10	50.07

The field experiment involved a variety of soils, i.e.

red soil (in Yixing), Shajiang black soil (in Xuyi), fluvo-aquic soil (in Huaiying and Xuzhou), salinized meadow soil (in Xiangshui), grey meadow soil (in Jiangdu) and coastal saline soil (in Guangyun).

8.1 Field experiment (part of the results)

8.1.1 Crop response on neutral and acid soils

In this experiment acid and slight acid soils were the red soil in Yixing, neutral soils (the Shajiang black soil) in Xuyi and the grey meadow soil in Jiangdu. Three treatments were designed as 1) No P (NK as CK); 2) 300kg/ha SP (superphosphate, containing 42.3kg/ha of citric acid soluble P_2O_5 and 45.9kg/ha of total P); 3) 300 kg/ha of PAPR (containing 27.9 kg/ha of citric acid soluble P_2O_5, and 55.65 kg/ha of total P). Results of the experiment are listed in Table 8 – 2.

Table 8-2 Crop response of PAPR on acid and neutral soils

Location	Yixing	Yixing	Xuyi	Jiangdu
Soil	Red soil	Red soil	Shajiang soil	Grey meadow soil
pH	5.5	5.6	6.7	6.7
Crop	Sweet potato	Milkvetch	Sesbania	Milkvetch
CK *	13.2a**	9.5a	6.1a	7.5a
SP *	17.8b	25.1b	10.4b	17.0b
PAPR *	17.3b	21.8b	9.5b	16.0b
Relative %	98	87	91	94

Note: * yield t/ha, Relative percentage with SP as basis: ** different letters signifies 5% significance in difference.

It is clearly shown in Table 8 – 2 that although the effectiveness of PAPR is only 87% ~ 98% that of SP, the difference is not statistically significant. Therefore, the PAPR used in the experiment can be considered equal to superphosphate in effectiveness.

8.1.2. Crop response on soils with pH > 7

Table 8 – 3 shows crop response to PAPR on soils with pH >7 and calcareous soils.

Table 8-3 Crop response on soils with pH > 7

Location	Guanyun	Huaiying	Tongshan	Xiangshui
Soil	Coastal saline soil	Saline meadow soil	Fluvo-aquic soil	Saline meadow soil
pH	7.3	8.0	8.5	9.1
Crop	Soybean	Rice	Wheat	Rice
CK	575.5*a	3150a	1837a	3720a
SP	1942.5b	5265b	2625b	6525b
PAPR	1260c	5175b	5175b	6345b
Relative %	65	98	94	97

Note: * yield kg/ha, Relative percentage with SP as basis: ** different letters designates 5% significance in difference.

It is clearly shown in Table 8 – 3 that similar to superphosphate, PAPR met with nice crop response from both rice and wheat on alkaline soils. But from soybean on coast saline soil, its crop response was only 65% of that of superphosphate and this difference was statistically. It can, therefore, be concluded that crop response of PAPR depends on a series of factors no matter whether on alkaline soil or calcareous soil. It can not be assumed that it always equalizes superphosphate.

8.1.3. Residual effect on calcareous soil

It is generally held that if the effectiveness of PAPR is lower than soluble P fertilizer on the current crop, its residual effect may be equal to the latter's. That is why we continued the experiment on the coast saline soil to the next crop without P application. Results of the experiment are listed in Table 8 – 4.

Table 8-4 Residual effect of PAPR on sweet potato in coast saline soil without P application in second crop

Treatment	Yield (t/ha)	Relative %
CK	11.8	--
Superphosphate	21.6	100
PAPR	17.2	80

The data in Table 8 – 4 indicated that on coast saline soil although the residual effect of PAPR was still lower, but rose from 65% to 80% that to superphosphate. The rise, however, is often the result of depletion of soluble P of the soluble P fertilizer. It is hard to infer that the relative effectiveness of PAPR in the residual effect rises.

8.2 Lab Experiments

8.2.1. Properties of PAPR of different acidulation degree (lab preparation)

PAPRs of different acidulation degrees were prepared in the lab with H_3PO_4 acidulating phosphate rocks low in reactivity from Jinping of Jiangsu and phosphate rocks moderate-minus in reactivity from Kunyan of Yunnan to five acidulation degrees (0, 10, 30, 50 and 100%). Properties of the end-products are listed in Table 8 – 5.

Table 8-5 Properties of PAPRs of different acidulation degree

Acidulation degree (%)	Total P_2O_5 (%)		2% Citric acid soluble P (P_2O_5 %)		Available P*/total P (%)	
	Jinping	Kunyang	Jinping	Kunyang	Jinping	Kunyang
0	29.1	29.8	0.73	5.2	2.5	17.4
10	37.1	36.9	11.4	16.0	31	43.4
30	45.9	44.0	25.8	30.5	56.2	69.3
50	52.1	49.3	38.0	43.8	73	88.8
100	55.7	55.1	85.0	56.0	100	100

*: Available P = 2% Citric acid soluble P

It is clearly shown in Table 8 – 5 that acidulation of phosphate rocks with H_3PO_4 greatly increased total P content in the end-product by 79% when the acidulation degree was kept at 50% and by 89% when the acidulation degree reached 100%. This is one of the major advantages of acidulation with H_3PO_4. The increase in available P was more significant. Available P accounted for 56% of the total P in rocks from Jinping and for 69% in rocks from Kunyang when they were acidulated to 30%. It is clear that when the rocks were acidulated with H_3PO_4 to 30%, available P had already rose beyond 50% of the total P.

8.2.2. Crop response to PAPRs of different acidulation degree (pot experiment)

PAPRs from two deposites of different acidulation degree prepared in the lab were used for pot experiment with rice and pea on acid red soil (pH 5.6) derived from the Quaternary red clay. Each pot had 6 kg of soil and was applied with 1.5g P_2O_5 (on the basis of total P_2O_5 in the fertilizer) for rice and 1g for pea. The crops were harvested when mature for rice and at the stage of full bloom for pea. The results of the pot experiment are listed in Tables 8 – 6 and 8 – 7.

Table 8-6 Crop response of rice to PAPRs of different acidulation degree

Acidulation degree	Jinping deposite		Kunyang deposite	
	Yield (g/pot)	Relative %	Yield (g/pot)	Relative %
CK	13.9	36	13.6	36
Raw rock powder	21.3	56	22.1	58
10%	32.5	85	32.8	86
30%	33.9	89	32.9	86
50%	—	—	33.0	86
100%	36.8	96	37.2	97
Superphosphate	38.2	100	38.2	100

Table 8-7 Crop response of pea to PAPRs of different acidulation degree

Acidulation degree	Yield (g/pot)	Relative %
CK	5.3	15
Raw rock powder	5.5	16
10%	26.0	76
30%	30.0	88
50%	33.5	98
100%	32.8	96
Superphosphate	34.2	100

Table 8 – 6 shows that when the acidulation degree of PAPR was 30% and even 50%, the crop response of rice to PAPR was less than 90% that to superphosphate, indicating that flooding increased soil pH, which might in turn affect crop response to PAPR because dissolution of the not-yet-reacted portion (or residue) of phosphate rocks was weakened. However, Table 8 – 7 shows that when the acidulation degree reached 50% (Jinping deposite), the crop response of pea to PAPR was almost the same as that to superphosphate. This may be because the soil was in an oxidizing condition and appeared acidic. In addition, leguminous crops are more able to make use of phosphate rocks. What is noteworthy is that, even in such a condition, the crop response of pea to PAPR 30% in acidulation degree failed to reach 90% that to superphosphate., which may be attributed to the low reactivity of the phosphate rocks. But when the acidulation degree reached 50%, the crop response of pea to PAPR was almost at the same level as that to superphosphate. All of these indicate that for rice it is better to have PAPR with higher acidulation degree and that when phosphate rocks low in reactivity are used, they should be acidulated at least to 50%, even with H_3PO_4.

8.2.3. Comparative crop response between PAPR and mixture of superphosphate and phosphate rock powder

In order to compare PAPR of chemical acidulation with PAPR of physical blending in crop response, samples of the materials similar in total P and available P contents were used in a test for that purpose. The soil used in the test was acid red soil and experiment was conducted on rice. The results of the test are listed in Table 8 – 8.

It is clearly shown in Table 8 – 8 that there was no big difference between PAPR prepared chemically with PAPR prepared by blending in crop response when they were similar in total P and available P contents. This means that they are quite similar in properties. Predecessors (Hagin, 1985) have confirmed that they are similar in composition. And this test is proof that they are approximate in crop response, too.

Table 8-8 Comparison between chemical acidulation PAPR and Physical blended PAPR in crop response

Treatment	PAPR of Chemical acidulation		PAPR of physical blending	
	Yield (g/pot)	Relative %	Yield (g/pot)	Relative %*
CK	8.0			
Raw rock powder (Jinping)	7.2			
10% **	15.6	100	14.4	92
30%	28.0	100	26.8	96
50%	33.3	100	31.7	96
100%	38.0			
Superphosphate	33.0			

*: The yield of PAPR of chemical acidulation is used as the base (100%).

** rate of acidulation degree

8.3 Some concluding remarks

The researches on PAPR done in the 1970s can be summarized with the following conclusions.

On acid and neutral soils, the crop response to PAPR 50% in acidulation degree is roughly equal to that to superphosphate.

On calcareous soils and soils with pH > 7, crop response to PAPR depends on a series of factors. Normally it will not be as high as that of soluble P fertilizer when its acidulation degree is 50%.

On calcareous soils, residual effect of PAPR is not significant.

Rice crop is less capable of utilizing phosphate rocks and in addition, flooding often makes pH rise in acid soils. As a result, application of PAPR 50% in acidulation degree to rice will hardly meet the same crop response as that of superphosphate.

When phosphate rocks low in reactivity, like those from Jinping are used, even if acidulated with H_3PO_4 to 50%, they will not get the same crop response from rice as compared to fully acidulated P fertilizers, but they may do from upland crops.

Chapter 9. Characteristics of the soils, phosphate rocks and PAPR in the Sino-French cooperative project

9.1 Properties of phosphate rocks for test

9.1.1. Chemical composition of the phosphate rocks for test

In this cooperative research project, involved were phosphate rocks from five phosphorate deposits. i.e. the Kunyang Deposit, Jinning Deposit, and Haikou Deposit (two kinds of phosphate rocks, one high in grade and the other low in grade) in Yunnan and the Shimen Deposit in Hunan.

At that time, the basic considerations for selecting phosphate rocks for the test were: 1) phosphate rocks moderate-minus in grade; 2) rocks moderate-minus in reactivity; and 3) the deposit fairly large in reserve. The three deposits in Yunnan were basically in consistence with the above conditions.

The choice of the Shimen Deposit was made mainly out of the consideration that the rocks in the deposit were not fit for the production of chemical P fertilizers (but fit for the production of Calcium Magnesium Phosphate fertilizer) because they were very high in MgO content (8.99% in contrast, it was only 0.20% in Kunyang and 0.85% in Jinning), but low in grade (only 16.86% in P_2O_5 content). Therefore, if phosphate rocks from that deposit can be used to produce PAPR, the production will pave a new way to utilize phosphate rocks of that kind. Nevertheless, out of a variety of causes (among them were time, funds and acid consumption of the rocks), the phosphate rocks from the Shimen Deposit were not used in the test of PAPR. So, only phosphate rocks from Kunyang, Jinning and Haikou were used. In Table 9 – 1 listed were mean chemical compositions of the phosphate rocks from Kunyang and Jinning and in Table 9 – 2 chemical compositions of the phosphate rocks from the three deposits actually used in the test.

Table 9-1 Mean chemical composition of the phosphate rocks from Kunyang and Jinning (20 samples, %)

Element	Kunyang			Jinning		
	Mean	SD*	CV*	Mean	SD	CV
P_2O_5	26.5	0.54	9.0	20.7	0.17	3.8
CaO	36.4	0.51	8.8	28.9	0.20	4.3
SiO_2	27.6	0.97	15.8	32.7	1.11	15.1
Al_2O_3	0.95	0.02	22.6	5.57	0.01	5.0
Fe_2O_3	0.92	0.02	19.7	1.37	0.01	6.5
MgO	0.21	0.006	21.3	1.12	0.025	16.4
K_2O	0.30	0.1	26.2	0.80	0.007	5.2
Na_2O	0.17	0.002	9.2	0.10	0.008	11.1
Mn	444	18.4	18.5	1154	14.6	5.6
Zn (mg/kg)	60	3.12	23.1	252	2.4	4.2
Cu (mg/kg)	16	0.68	18.9	24	0.88	24

*: SD stands for standard deviation and CV for coefficient of variation.

Table 9-2 Chemical composition of phosphate rocks used in the test (%)

Element	Kunyang	Jinning	Haikou*	
			High in grade	Low in grade
P_2O_5	26.3	20.4	29.16	18.87
CaO	35.8	27.1	37.71	24.82
SiO_2	28.8	36.2	20.43	40.55
Al_2O_3	0.99	2.65	3.21	2.51
Fe_2O_3	0.96	1.40	1.59	1.26
MgO	0.21	1.17	0.30	0.23
K_2O	0.31	0.81	0.54	0.48
Na_2O	0.18	0.10	0.18	0.12
MnO	0.06	0.16	0.15	0.08
CO_2	0.61	1.98		
S	0.15	0.07	<0.05	<0.05

*: This is only the general chemical composition of the phosphate rocks from Haikou. Please refer to Table 9 – 10 for total P content in the phosphate rocks used in the test.

The mean total P content of the phosphate rocks from the Kunyang Deposit was 26.5%, from the Jinning Deposit 20.7% (Table 9 – 1) and 29.1% and 18.87% from the Haikou Deposit (Table 9 – 2). According to the prevalent criteria for classification, phosphate rocks with total P content > 30% are high in grade, between 24% and 30% moderate in grade and < 24% low in grade. Therefore, the Kunyang Deposit is of moderate grade, the Jinning Deposit of low grade and the Haikou Deposit of moderate and low grade (Table 9 – 2). So they satisfied our original targets.

Although the Kunyang, Jinning and Haikou Deposits are not high in P content, they are not high either in Fe, Al and Mg contents. Manufacturing P fertilizers with wet process requires that phosphate rocks of the first grade should be < 10.0% in MgO/ P_2O_5, <15.0% in R_2O_3/ P_2O_5 and < 7% in CO_2. The phosphate rocks from the three deposits meet all these requirements. Therefore, the rocks from the three deposits are suitable not only for production of PAPR, but also for production of chemical P fertilizers after proper ore beneficiation. There is no wonder why Yunnan is an important phosphate base of China.

9.1.2. Reactivity of phosphate rocks for the test (index of agricultural effectiveness)

Besides the factors of P content and impurities, reactivity of the phosphate rocks is also an important factor for production of PAPR (please refer to Chapter 14). Because of that, reactivity of the phosphate rocks from the three deposits was determined. As the reactivity of phosphate rocks is closely related to crop response to direct application of phosphate rock powder, it is also termed as "index of agricultural effectiveness”.

Usually, there are four methods that can be used to determine reactivity of phosphate rocks, i.e.

- the neutral ammonium citrate method (the A.O.A.C.method, second extraction);
- pH 3 acidic ammonium citrate method
- 2% citric acid method;
- 2% formic acid method.

It is generally held that the first method is best related to crop yield. But the third method is commonly used in China and the fourth in Europe. Researches (Leon et al., 1986; Chien et al., 1978), however, indicate that besides the first method, the other three methods are also closely related to crop response. Table 9 – 3 shows grading of the four methods by Leon (1986).

Table 9-3 Grading of reactivities of phosphate rocks (index of agricultural effectiveness)

Method	High (94)*	Moderate (76)	Low (55)	Ext. Low (21)
1. Extraction with neutral ammonium citrate				
% of the rocks	2.6	1.2	0.5	0.2
% of total P	18.6	11.2	4.3	1.3
2. Extraction with pH 3 ammonium citrate				
% of the rock	10.9	4.5	2.0	0.6
% of total P	77.9	40.6	16.7	3.6
3. Extraction with 2% citric acid				
% of the rock	5.8	2.9	2.5	1.3
% of total P	41.6	25.6	23.3	8.0
4. Extraction with 2% formic acid				
% of the rock	9.1	3.1	2.2	1.4
% of total P	65.7	28.0	19.1	9.1

*: The figures in the parentheses stand for effectiveness (%) of chemical P fertilizer

The indexes in Table 9 – 3 are mean values, of which each has actually a range of variation. In addition, they are also expressed in two ways. One is percentage of the amount extracted against the amount of the phosphate rocks and the other is the amount extracted against the content of total P in the rocks. Based on the two indexes, the same phosphate rocks may not be sorted into the same grade. So it is necessary to select which index to be used in light of the local conditions. Table 9 – 4 shows the result of sorting of the phosphate rocks for the test based on % of the rock.

It is clearly shown in Table 9 – 4 that the phosphate rocks from Jinning were determined low in reactivity with all the three methods whereas the rocks from Kunyang low with two methods and moderate with the other. Consequently, the rocks from Jinning are in the category of "Low" and rocks from Kunyang in the cateegory of "Moderate – Low", which is in consistence with the experience we had.

Table 9-4 Grading of phosphate rocks from Kunyang and Jinning in terms of reactivity (index of agricultural effectiveness)

Extractant*	Kunyang			Jinning		
		%/total P			%/total P	
	%/rock	%	Grade	%/rock	%	Grade
Water	0.26	0.10	-	0.22	0.11	-
NAC	1.9	7.2	Low	1.4	6.8	Low
2%CA	6.2	23.7	Low	4.7	23.1	Low
2%FA	7.8	29.8	Moderate	5.1	25.2	Low
SS(m^2/g)	3.7	-	-	1.22	-	-

*: NAC stands for neutral ammonium citrate; CA for citric acid; FA for formic acid; and SS for specific surface.

The phosphate rocks of high grade from Haikou are low in reactivity (by neutral ammonium citrate method) but moderate with low grade rocks (Table 9 – 10).

For the sake of comparison, reactivity grading of phosphate rocks from other countries is listed in Table 9 – 5. It is clearly shown that the rocks from North

Carolina of the USA and from Gafsa of Tunisia fall into the category of "High", which is in conformity with the characteristics of the world's famous phosphate rocks, high in reactivity. In comparison with that of the phosphate rocks from Kunyang, the amounts of P extracted from these rocks with the three different extractants are 2 ~ times higher.

Table 9-5 Reactivity indexes of phosphate rocks from other countries (% of total P)

Deposit	NAC*	2%CA*	2%FA*
North Carolina, USA	22.3(high)	53.1(high)	86.3(high)
Gafsa, Tunisia	18.5(high)	47.0(high)	74.6(high)
Khoribga, Morocco	14.5(moderate)	24.3(moderate)	34.3(moderate)
Hahotoe, Togo	8.3(low)	20.1(extremely low)	39.8(moderate)

*: NAC stands for neutral ammonium citrate; CA for citric acid; and FA for formic acid.

Specific surface is another index of reactivity for phosphate rocks. It determines not only contact area of phosphate rock powder with soil (the larger the contact area, the more effectiveness of the rock), but also the contact area with acid during the process of the production.

The specific surface of phosphate rocks consists of internal and external specific surfaces and mainly of the former. This is a natural attribute of phosphate rocks. The larger the internal specific surface, the higher the porocity, the lower the density (specific weight), and the higher the reactivity. It is positively related to lattice isomorphous replacement (lattice cell parameters) of the rocks. The external surface, however, is often affected by artificial grinding.

Moroccan phosphate rocks, highest in reactivity, have a specific surface of 17.99 m^2/g. According to Table 9 – 4, the specific surface of Kunyang phosphate rocks is

3.7 m^2/g and of Jinning phosphate rocks only 1.22 m^2/g, which is only 20% and 7%, respectively, that of Moroccan phosphate rocks.

9.2 Preparation, characteristics and acidulation efficiency of PAPR

9.2.1. Preparation of PAPR and available P content of the product

In this paragraph no space will be spared for technology of the production of PAPR. Please refer to Chapter 6 for details of this aspect. What is addressed here is what kind of acid and how much is to be used in production of PAPR, and hence general information about every product.

During the test, a total of 12 kinds of PAPR were prepared. Table 9 – 6 shows kind, concentration and amount of the acid used to prepare each product.

Table 9-6 Kinds and amounts of acids used to prepared PAPR out of phosphate rocks from two deposits

Serial No.	Code*	Kind of acid used	Concentration of acid(%)	Amount used (kg/100kg dry rock)	
				Kunyang	Jinning
C.1.1	S30	H_2SO_4	48.5	27.2	24.0
C.1.2	S60	H_2SO_4	65.3	40.3	35.4
C.1.3	P30	H_3PO_4	35.0	28.8	25.4
C.1.4	P60	H_3PO_4	45.0	44.9	39.6
C.1.7	SP30	H_2SO_4	48.5	13.6	12.0
		H_3PO_4	35.0	14.4	12.7
C.1.8	SP60	H_2SO_4	65.3	20.1	17.7
		H_3PO_4	45.0	22.5	19.9
C.1.9	SN3	H_2SO_4	48.5	13.6	12.0
		HNO_3	56.0	7.6	6.7
C.1.10	C.1	H_2SO_4	5.0.	21.0	18.5
		MAP*	-	11.0	9.7
C.1.12	C.3	H_2SO_4	50	21.0	18.5
		MAP	-	11.0	9.7

*: S stands for H_2SO_4, P for H_3PO_4, “30” and “60” for acidulation degree, C for compound fertilizers and MAP for monoammonium phosphate.

In the test, three kinds of acid were used, phosphoric, sulfuric and nitric acids, among which phosphoric acid was the best in dissolving phosphate rocks. When Kunyang phosphate rocks were acidulated to 30% (P30) with phosphoric acid, the product had soluble P about 50% of its total P and when up to 60% (P60), it had 73%. Of course, phosphoric acid contains P per se. Taking into account the price and dependence-on-export of phosphoric acid in China, a mixture of H_2SO_4 and H_3PO_4 was tested with fairly good result. When the rocks were acidulated to 30% (SP30) soluble P accounted for 38% of the total P and when to 60% (SP60), for 67%.

With price of the product put under consideration, H_2SO_4 was used as acidulating agent. When the rocks were acidulated to 30% (S30) soluble P accounted for 21.3% of the total P and when to 60% (S60), for 27.9%.

In the test HNO_3 was also tried for two reasons. One was that the price of HNO_3 was relatively cheap and the other that it might increase N content in the product. Nevertheless, HNO_3 was not so good at dissolving phosphate rocks. When the rocks were acidulated to 30%, soluble P accounted only for 13.5% of the total P. P extracted of the phosphate rocks from the two deposits, Kunyang and Jinning with different acidulating agents were listed in Tables 9 – 7 and 9 – 8.

In the test a mixture of H_2SO_4 and MAP was also tried with the purpose of saving acid and introducing in N.

Table 9-7 Available P contents of PAPRs from Kunyang phosphate rocks

Code*	Total P_20_5 (%)	P extraction with different method (% of total P_20_5)							
		Extraction for half an hour				Extraction for two hours			
		Water	NAC*	CA*	FA*	Water	NAC	CA	FA
Raw rock	26.3	0.08	5.3		25.75	0.10	7.29		29.8
S30	22.2	21.3	27.8	39.1	35.1	21.3	28.0	44.2	36.6
S60	18.8	27.9	60.8	63.0	58.9	27.9	60.9	69.2	62.0
P30	34.8	54.1	54.4	58.8	55.3	49.7	55.7	60.1	56.4
P60	40.0	73.8	77.1	74.7	78.9	73.2	78.7	76.7	75.9
SP30	29.8	39.0	42.3	50.9	46.0	38.5	43.7	53.0	46.3
SP60	31.4	66.0	68.9	69.7	68.5	67.0	71.2	72.0	67.8
SN30	22.6	13.4	17.9	33.2	31.4	13.5	18.0	37.3	33.0
C1	24.2	29.7	34.7	47.6	42.9	29.7	36.2	52.0	43.0
C3	23.5	31.6	35.5	49.9	42.1	32.7	35.7	54.0	43.5

*: The same as in Table 9 – 5.

Table 9-8 Available P contents of PAPRs from Jinning phosphate rocks

Code*	Total P_20_5 (%)	P extraction with different method (% of total P_20_5)							
		Extraction for half an hour				Extraction for two hours			
		Water	NAC*	CA*	FA*	Water	NAC	CA	FA
Raw rock < 160μ	20.4	0.10	5.20		23.29	0.11	6.80		25.26
< 63μ	16.9	0.12	7.07		23.87	0.12	8.67		24.48
S30	19.1	16.0	20.9	34.3	31.0	16.7	21.2	40.9	34.5
S60	16.9	34.0	41.8	54.1	41.4	34.8	42.8	63.4	45.0
P30	31.1	42.9	47.3	58.2	49.9	43.1	51.6	61.0	53.5
P60	34.9	70.0	78.7	79.5	77.2	72.1	81.8	81.2	76.5
SP30	25.3	32.6	37.6	49.7	42.8	33.4	37.3	53.5	46.0
SP60	28.4	58.8	64.2	69.0	63.5	59.1	64.6	72.2	63.8
SN30	19.3	10.7	15.9	32.6	27.5	10.7	16.1	37.2	31.9
C1	21.4	24.1	30.8	47.0	37.1	25.0	31.2	51.2	40.6
C3	20.2	29.7	33.8	50.5	41.9	29.8	33.8	54.4	46.1

*: The same as in Table 9 – 5.

In Tables 9 – 9 and 9 – 10, listed are data about PAPR preparation from phosphate rocks of Haikou and available P contents in the resultant products. Table 9 – 9 shows clearly that phosphate rocks of low grade, from Haikou were acidulated mainly with mixed acid (H_2SO_4 + H_3PO_4) and to a higher acidulation degree. The use of the mixture was aimed at raising available P content in the product.

Table 9-9 Preparation of PAPR from Haikou phosphate rocks

Code *	Acid	Concentration (%)	Consumption (kg/100kg rocks)
H45	H_2SO_4	80	13.6
	H_3PO_4	53	14.8
H75	H_2SO_4	80	21.3
	H_3PO_4	53	24.7
HC33	H_2SO_4	80	20.3
	MAP	-	12.6
L45	H_2SO_4	80	9.2
	H_3PO_4	53	10.0
L75	H_2SO_4	80	15.3
	H_3PO_4	53	16.7
LC33	H_2SO_4	80	13.6
	MAP		8.6

*: H stands for high in grade, L for low in grade, C for complex treatment, MAP for monoammonium phosphate and the figure after the letter or letters for acidulation degree.

Table 9-10 Available P content of PAPR from Haikou phosphate rocks (% of total P)

Code*	Total P_2O_5 (%)	Water		NAC*		CA*	
		1/2 hr	2 hrs	1/2 hr	2 hrs	1/2 hr	2 hrs
Rock-H	24.77	0.22	0.22	8.0	9.9	24.6	28.0
H45	26.42	39.6	39.6	44.9	44.9	56.2	58.4
H75	27.38	60.6	61.7	67.4	67.4	69.3	72.3
HC33	25.42	26.3	36.3	41.7	41.7	51.7	56.8
Rock –L	22.87	0.25	0.25	9.2	11.5	26.6	29.8
L45	23.88	30.6	31.0	36.3	36.5	41.4	52.7
L75	24.09	51.2	53.5	59.5	59.5	63.6	69.1
LC33	22.02	25.4	26.4	34.4	36.8	48.1	53.0

*: H stands for high grade, L for low grade, C for complex treatment, NAC for neutral ammonium citrate and CA for citric acid.

9.2.2. Rate of acidulation efficiency in producing PAPR

The so-called efficiency acidulation rate of PAPR has two meanings: one is calculated on the basis of its water soluble and the other on the basis of NAC soluble P.

Rate of acidulation efficiency (water soluble P)

$$= \frac{\text{Water soluble P(\%)}}{\text{Total P(\%) in product x acidulation degree(\%)}} \times 100$$

Rate of acidulation efficiency (Available P)

$$= \frac{\text{NAC soluble P \% + water soluble P(\%)}}{\text{Total P(\%) in product x acidulation degree(\%)}} \times 100$$

It can be inferred from the above two equations that the efficiency acidulation rate refers to the ratio of the actual amount of P transformed to water soluble P against the amount of P theoretically transformed, i.e. the efficiency of water soluble P. As in the production, some water soluble P is turned into insoluble P, but can be dissolved by NAC, efficiency acidulation rate is then calculated on the basis of NAC. Based on the above two equations, efficiency acidulation rates of phosphate rocks from Kunyang and Jinning were calculated with results listed in Table 9 – 11.

Table 9-11 Efficiency acidulation rates of the test

Phosphate rocks	Acid used	Acidulation degree (%)	Efficiency acidulation rate (%)	
			Based on water soluble P	Based on NAC soluble P
Kunyang	H_2SO_4	30	71	93
		60	47	98
	HNO_3	30	45	60
Jinning	H_2SO_4	30	56	71
		60	58	71
	HNO_3	30	37	54

It is clearly shown in Table 9 – 11 that the reactivity of phosphate rocks from Kunyang is higher than that from Jinning and that so is the efficiency acidulation rate. So to produce PAPR, rocks higher in reactivity consume less acid. The table also shows that HNO_3 is lower than H_2SO_4 in efficiency acidulation rate, in particular, on the basis of water soluble P.

9.2.3. Mineral composition of PAPR

In the test, x-ray diffraction patterns were used to identify PAPR products. Here only the pattern of the product (SP60) from Kunyang phosphate rocks acidulated with $H_2SO_4 + H_3PO_4$ to 60% is cited (Fig. 9 – 1). The pattern clearly shows that besides some phosphate rock residues and SiO_2, the product contained some $Ca(H_2PO_4)\cdot H_2O$, $CaSO_4\cdot 2H_2O$ and a limited amount of $CaHPO_4$; In the sample of C.1.12 product there was some monoammonium phosphate (not published yet), which indicates the proportion of monoammonium phosphate turned into $(NH_4)_2SO_4$ was limited.

In addition, CIRAD also had PAPRs from phosphate rocks of Kunyang and Jinning determined for mineral composition with results listed in Table 9 – 12.

Table 9-12 Minerals in PAPR

Mineral	Product from Kunynag rocks				Product from Jinning rocks			
	S30	S60	SN30	C.1	S30	S60	SN30	C.1
Apatite	**	*	**	*	**	*	**	*
Quartz	**	**	**	*	**	*	**	*
Muscovite					(*)		(*)	
Mica					(*)		(*)	
$CaSO_4\cdot 2H_2O$	*	*		*		*		**
$Ca(H_2PO_4)_2\cdot H_2O$	(*)	*	*					
$CaNH_4PO_4$				*				

Note: * stands for existence and ** for higher in content.

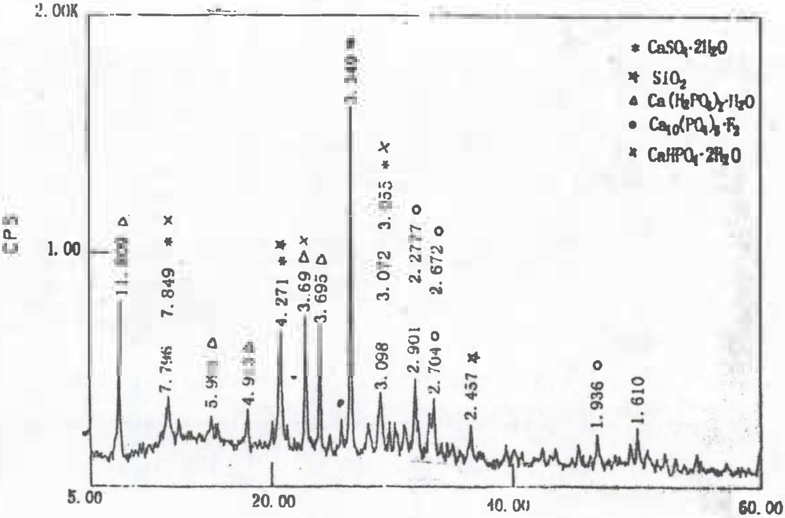

Fig. 9 – 1 X-ray diffraction pattern of SP60

It is known from the above table that quartz remained intact and apatite reduced significantly under H_2SO_4 treatment when rocks were acidulated.

In Jinning rocks, some muscovite and mica were dissolved when the rocks were acidulated, which wasted some acid.

In PAPR from Kunyang rocks, $Ca(H_2PO_4)_2$ and soluble $CaNH_4PO_4$ did not exist in PAPR from Jinning rocks, maybe it could not be detected by X-ray.

9.3 Properties of major soils in field experiments

9.3.1. Soils used and field experiments

For this research project, 22 field experiments were carried out in the years before 1990, 19 experiments in 1991 and 24 experiments in 1992 of PAPRs from Haikou phosphate rocks. Of the 24 experiments 7 were designed for study of residual effect. So there were a total of 65 field experiments were conducted. At the same time, 6 pot experiments were performed in China and some others in France, too.

The soils used in the test were mainly acid upland soils in South China, and some other calcareous soils and paddy soils, too. Basic information about some of the soils are listed in Table 9 – 13. It is shown that the soils are mainly red soils distributed in Zhejiang, Jiangxi, Hunan and Yunnan, fluvio-aquic soils distributed widely in the North China Plain in Henan and paddy soils from Jiangsu.

Table 9-13 Basic information about the soils for test

Soil No.	Soil	Collection site	Type of experiment
1	Paddy soil*	Liyang, Jiangsu	Pot ex., Kunyang, Jinning PAPR
2	Red soil	Yujiang, Jiangxi	Pot ex., Kunyang, Jinning PAPR
3	Fluvio-aquic soil (clayey)	Fengqiu, Henan	Pot ex., Kunyang, Jinning PAPR
4	Red soil	Shanggao, Jiangxi	Soybean, field experiment
5	Red soil	Jinhua, Zhejiang	Soybean, field experiment
6	Red soil	Yingtan, Jiangxi	Peanut, field experiment
7	Red soil	Jinxian, Jiangxi	Sesame, field experiment
8	Red soil	Yunnan	Pot experiment
9	Red soil	Zhejiang	Pot experiment
10	Fluvio-aquic soil	Fengqiu, Henan	Sesame, field experiment
11	Red soil	Jiujiang, Jiangxi	Soybean, field experiment
12	Red soil	Shanggao, Jiangxi	Soybean, field experiment
13 – 15	Red soil	Zhejiang	Soybean, field experiment
16	Red soil	Dongyang, Zhejiang	Corn, field experiment
17	Red soil	Ningxiang, Hunan	Soybean, field experiment
18	Paddy soil	Liyang, Jiangsu	Rapeseed, field experiment

* derived from yellow brown soil

9.3.2. Basic properties of the soils in experiments

These soils were all very low in P content (Table 9 – 14). With available P ranging between 1 ~ 9.5mg/kg, they were basically in the category of soils deficient in P. In Table 9 – 13, listed are also results of the determination of available P with the Olsen-Dabin method, which is rarely used in China, but common in France. It is indicated in the table that of the same soil the available P content is much higher when the Dabin method is used than when the Olsen method is used. This may be the advantage of the former.

Table 9-14 P status of soils for test

No.	Soil	Total P %	Available P (Olsen) (mg/kg)	Olsen-Dabin-P (mg/kg)
1	Paddy soil (Liyang)	0.023	1.9	11.0
2	Red soil (Yunjiang)	0.018	1.0	6.5
3	Fluvio-aquic soil (Fengqiu)	0.060	1.2	30.4
4	Red soil (Shanggao)	0.037	4.3	35.6
5	Red soil (Jinhua)	0.047	9.5	53.7
6	Red soil (Yingtan)	0.038	4.8	46.5
7	Red soil (Jinxian)	0.020	4.6	16.3
11	Red soil (Jiujiang)	-	8.7	-
16	Red soil (Dongyang)	-	5.0	-
17	Red soil (Ningxiang)	-	5.5	-

The soils for test also varied sharply in texture with clay contents ranging from 13.3% to 45.6% (Table 9 – 15) and so did they in exchange capacity (Table 9 – 16). For instance, their ECE varied from 3.92 cmol/kg to 14.7 cmol/kg. All these indicate that the soils used in the test do have their representativeness. Listed in Table 9 – 17 are general chemical properties. It shows pH (H_2O) ranging from 3.65 to 8.45. So all the soils were acid soil (weakly or strongly acid), except the fluvio-aquic soil from Henan, which is calcareous soil. This is because PAPR is more fit for acid soils.

Table 9-15 Physical properties of the soils for test* (%)

No.	Soil	Clay	Fine silt	Coarse silt	Fine sand	Coarse sand
1	Paddy soil (Liyang)	26.2	43.3	27.3	1.6	1.7
2	Red soil (Yunjiang)	32.0	20.4	11.3	29.4	7.0
3	Fluvio-aquic soil (Fengqiu)	28.3	32.0	25.8	13.1	0.8
4	Red soil (Shanggao)	37.6	31.1	9.3	17.1	5.0
5	Red soil (Jinhua)	34.0	42.9	14.0	4.3	4.8
6	Red soil (Yingtan)	45.6	21.1	9.2	14.2	10.0
7	Red soil (Jinxian)	13.3	18.1	16.0	28.8	23.8

*: The textures were determined with the French method.

Table 9-16 Exchange capacity of the major soils for test (cmol/kg)

Element (Exchgnge)	Soil (location)						
	Liyang	Yujiang	Fengqiu	Shanggao	Jinhua	Yingtan	Jinxian
Ca	8.76	0.62	11.56	6.88	2.94	1.13	2.65
Mg	3.04	0.27	3.04	2.15	0.58	0.47	0.91
K	0.16	0.12	0.32	0.32	0.07	0.15	0.08
Na	0.15	0.54	0.55	0.08	0.03	0.01	0.01
Al	0.01	6.73	0.00	0.70	0.35	1.94	0.27
Mn	0.41	0.0	0.00	0.17	0.02	0.05	0.30
H	0.01	0.18	0.00	0.07	0.05	0.11	0.07
Total	12.54	8.46	15.47	10.37	4.04	3.86	4.29
CEC	13.07	9.22	14.70	10.35	4.00	3.92	4.24
Saturation %*	96	92	105	100	101	98	101

* Saturation % = cation total/CEC·100

Table 9-17 Chemical properties of the major soils for test

Properties	Soil (location)						
	Liyang	Yujiang	Fengqiu	Shanggao	Jinhua	Yingtan	Jinxian
OM %	1.65	0.84	1.44	1.72	1.82	1.79	1.12
N g/kg	0.99	0.52	0.80	1.16	1.15	0.96	0.72
C/N	9.70	9.40	8.30	8.60	9.2	10.80	9.00
Ca*	18.4	2.83	295.98	8.84	10.1	5.14	7.34
Mg*	26.2	40.88	110.72	51.17	20.31	25.78	18.73
K*	30.9	35.75	51.41	37.16	22.68	22.31	17.87
Na*	39.9	3.18	45.29	3.98	3.65	2.53	2.52
Fe %	2.51	3.42	3.42	4.37	2.93	3.93	2.82
Al %	5.90	6.90	3.28	7.68	5.85	7.85	3.65
pH (H_2O)	5.75	5.30	8.45	5.45	5.35	4.85	
pH (KCl)	4.89	4.05	7.50	4.40	4.45	4.05	

* cmol/kg

Chapter 10. Effectiveness of PAPR on acid soil

10.1 Briefing on the experiment

The experiment project consisted of portions, field experiments and pot experiments. The field experiments were laid and carried out in five provinces (Table 10 –1), and the pot experiments in Nanjing.

10.1.1. Field and pot experiments before 1990

As is shown in Table 10 – 1, a total of 22 field experiments were conducted before 1990. Among them, 6 were experiments on residual effect.

The soils of the field experiments were red soil, except the one in Liyang of Jiangsu. For information about properties of some of the soils, please refer to Paragraph 9.3 of Chapter 9 and Paragraph 10.2 of this Chapter.

In 1990, a total of six pot experiments were carried out with soils coming from Jiangxi (red soil), Yunnan (red soil), Zhejiang (red soil), Jiangsu (paddy soil) and Henan (2 types of fluvio-aquic soils). For information about their properties, please refer to Table 10 – 4 and Table 9 – 16. The crop use for the pot experiments was ryegrass.

Table 10-1 Field experiments before 1990 (22 experiments)

Location	Crop		
	1st crop	2nd crop	2nd experiment*
Jiangxi province			
Yingtan	Peanut	Buckwheat	Buckwheat
Jinxian	Sesame	Rapeseed	Rapeseed
Shangrgao	Soybean	-	-
Shanggao	Sweet potato	Rapeseed	-
Xinjian	Soybean	-	-
Jiujiang	Sesame	Rapeseed	Rapeseed
Zhejiang province			

Location	Crop		
	1st crop	2nd crop	2nd experiment*
Jinhua	Soybean	Rapeseed	-
Jinhua	Soybean	Rapeseed	-
Jinhua	Soybean	-	-
Dongyang	Corn	-	-
Hunan province			
Ningxiang	Soybean	-	-
Guangdong province			
Huazhou	Soybean	-	-
Jiangsu province			
Liyang			Rapeseed

* P fertilizers were applied again in the same field, but no P fertilizers for the second crop.

10.1.2. Field and pot experiments on PAPR from Kunyang and Jinning phosphate rocks after 1990

Table 10 – 2 shows field experiments were carried out after 1990 and some of them were continuation of the experiments in 1990.

It is shown in Table 10 – 2 that after 1990 a total of 19 experiments were carried out and 7 of them on residual effect.

Originally a total of 25 field experiments were laid out after 1990. among them 4 failed to show any crop response because the soils were too high in available P content and 2 did too due to droughts. So, only 19 experiments were taken into account in the summary. The field experiments were distributed in five provinces, involving 10 species of crops.

Table 10-2 Field experiments after 1990

Location	Crop		
	1st crop	2nd crop	2nd experiment*
Jiangxi province			
Yingtan	Peanut	Buckwheat	Rapeseed
Jinxian	Sesame	Rapeseed	-
Jinxian	Rapeseed		-
Shanggao	Soybean	-	-
Shanggao	Sweet potato	Rapeseed	-

Location	Crop		
	1st crop	2nd crop	2nd experiment*
Jiujiang	Sesame	-	-
Jiujiang	Rapeseed	Rapeseed	-
Zhejiang province			
Jinhua	Soybean	Rapeseed	-
Jinhua	Corn		-
Dongyang	Corn	-	-
Hunan province			
Ningxiang	Broad bean	-	-
Jiangsu province			
Liyang	Rapeseed	Rice	-

The area of a plot in the experiments varied with the size of the farmer's field, generally ranging from 20 to 30 m^2. each experiment had four replicates and was designed to have a P_2O_5 application rate of 75kg/ha. N and K fertilizer were applied at a usual rate and a bit less on leguminous crops. In some fields lime and Zn, Mo, and B fertilizers were used. The pot experiments started before 1990 and continued through 1990 and on. A total of six harvests were made. All the P treatments received 120 mg P per kg soil with some addition of N, K, Mg and B. each pot had 1.5 kg of soil.

10.1.3. Field experiments on PAPR from Haikou phosphate rocks in 1992

Listed in Table 10 – 3 is some information about the field experiments on PAPR out of Haikou phosphate rocks carried out in 1992.

Table 10-3 Field experiments on PAPR from Haikou phosphate rocks (24 experiments)

Provinces	County	1st crop	2nd crop
Jiangxi	Jinxian	Peanut	Rapeseed
	Dongxiang	Sesame	-
	Xinjian	Peanut	-
	Xiajiang	Peanut	Rapeseed
	Shanggao	Soybean	Rapeseed
Zhejiang	Jinhua	Soybean	Rapeseed
	Jinhua	Soybean	-
	Lanxi	Soybean	-

Provinces	County	1st crop	2nd crop
Jiangsu	Pujiang	Corn	-
	Jurong	Corn (forage)	Corn (forage)
	Jurong	Rapeseed	-
	Liyang	Rice	Wheat
Henan	Shangqiu	Corn (5 trials)	Wheat
Total		17	7

10.2 Properties of soils for test

Properties of the soils for test have already been discussed in Chapter 9. In table 10 – 4 are listed supplementary data about the basic properties of some of the soils.

Table 10-4 Basic properties of some of the soils for test

Soil	Location	Crop	pH	OM (%)	TN (%)	mg/kg	
						Ex. K	Olsen P
Red soil	Quiqin, Yunnan	Ryegrass*	6.2	-	0.11	224	5.0
Red soil	Jinhua, Zhejiang	Ryegrass*	5.4	1.1	0.06	42	3.3
Red soil	Yingtan, Jiangxi	Peanut	4.5	1.9	0.10	82	4.8
Red soil	Jinxian, Jiangxi	Sesame	4.9	1.3	-	30	4.5
Red soil	Jiujiang, Jiangxi	Sesame	5.9	-	0.06	38	4.7
Red soil	Shanggao, Jiangxi	Soybean	5.0	1.8	-	85	4.0
Red soil	Shanggao, Jiangxi	Sweet potato	6.6	1.9	0.11	74	4.3
Red soil	Jinhua, Zhejiang	Soybean	5.5	2.0	-	34	9.5
Red soil	Kaihua, Zhejiang	Soybean	5.0	1.6	-	58	9.8
Red soil	Jinhua, Zhejiang	Soybean	5.2	1.6	-	104	1.4
Red soil	Jinhua, Zhejiang	Corn	5.0	2.3	-	105	5.0
Red soil	Ningxiang, Hunan	Mung bean	5.1	-	-	55	5.5
Paddy soil	Jurong, Jiangsu	Rapeseed	6.0	1.4	-	60	5.3

* pot experiments

10.3 Results of the field experiments

This experiment project had a total of 65 field experiments, among which 19 were designed for residual effect and 48 for current crops, involving 10 species of crops. The soils used in the experiments were mainly red soils except some individuals, which were paddy soils. The project had also 6 pot experiments (not including the pot experiments conducted in France), with 6 harvests of the test plant ryegrass.

Table 10-5 Responses of the current crops in 17 field experiments to the PAPRs prepared from Kunyang and Jinning phosphate rocks (1989 – 1992)

Fertilizer	Relative effectiveness (%)		
	1990 (4 experiments)	After 1990 (13)	Total (17)
SSP*	100	100	100
SP60K	94	93	93
C1K	96	93	94
SP60J	96	96	96
C1J	94	95	95
Mean	95	94	95

* K – Kunyang, J – Jinning, also see foot note in table 10 – 6.

Table 10-6 Responses of the current crops in 10 field experiments to the PAPRs prepared from Haikou phosphate rocks

Fertilizer *	High in grade	Low in grade	Total
SSP	100	100	100
SP45H	91	98	98
SP75H	100	101	100
C33	94	98	96
Mean	95	99	97

* SSP stands for superphosphate; SP45H for phosphate rocks from Haikou acidulated with mixed acid to 45% degree, C - treatment with H_2SO_4 + MAP

Listed in Tables 10 – 5 to 10 –6 are results of 27 field experiments. It is clearly shown that the relative effectiveness (with effectiveness of superphosphate as 100%) of the PAPRs prepared from phosphate rocks from the three deposits was more or less the same as that to a fully acidulated P fertilizer equal in total P and that there was no significant difference between the PAPRs.

Table 10 – 7 indicates that water soluble P accounted for 30% ~ 60% of the total P in the PAPRs and citrate soluble P for 50% ~ 70%. From the results of the field experiments, it can be inferred that on acid red soils in South China, PAPR should have water soluble P accounting for over 30% of its total P and citrate soluble P for 50% and be acidulated to over 50% with sulfuric acid and around 50% with mixed acid (H_3PO_4 + H_2SO_4). Such PAPRs would be similar to superphosphate, a fully acidulated fertilizer, in crop response.

Table 10-7 Contents of water soluble P and citrate soluble P in the PAPRs (% of total P)

Fertilizer	Water soluble P	Citrate soluble P
S60K	27.9	69.2
S60J	34.8	63.4
C1K	29.7	52.0
C1J	25	51.2
H45H	39.6	58.4
H75H	60.6	72.3
L45H	31	52.7
L75H	53.3	69.1

What is especially noteworthy is that the phosphate rocks from the 3 deposits all fall into the category of “medium-minus” in grade in terms of total P and between medium and low in reactivity. As long as PAPR products out of such phosphate rocks may reach the above-described standard, that is, they are similar to a fully acidulated fertilizer in crop response, the experiments are of tremendous significance to the utilization of medium- and low-grade phosphate rocks.

As phosphate rocks from the 3 deposits are quite low in content Fe, Al and Mg impurities that will affect the quality of their PAPR products, it is hard for us to make any judgment as to what will be the permissible range of the impurity content in the PAPR.

10.4 Variation of crop response to PAPR from soil to soil and its causes

It should be noted that the data Table 10 – 5 and 10–6, are the mean values of relative crop response of the 27 experiments. It fact each of them, phosphate rocks from every deposit and every type of PAPR, has a range of variation in relative effectiveness. In the case of the entire experiment, its range of variation was between 80% ~ 120%. Take for example that field experiments on PAPRs out of Kunyang and Jinning Deposits before 1990.

About 40% of the total experiments had a relative effectiveness ranging between 80 – 90% of SP60K while 60% of the experiment exceeded 90% of relative efficiency.

All the C1K had relative effectiveness higher than 90%. SP60J and C1J were the same as SP60K. Causes of the variations differ and are associated with a number of factors among which soil properties (pH and P fixation capacity) and acidulation degree of PAPR are major ones. Discussion of the two will be performed in the following paragraph.

10.4.1. Crop response to PAPR varying on 3 different red soils

In Tables 10 –8and 10 – 9 listed are crop responses to PAPRs on red soils from 3 different locations, Yujiang of Jiangxi, Jinhua of Zhejiang and Qujing of Yunnan province.

On the red soil from Jiangxi, crop response was obviously associated with the acidulation degree of PAPR (Table 10 – 8). The association was more obvious in the first harvest (Table 10 – 11). When the PAPR was at 30% in acidulation degree, its crop response was only 46% and when at 60%, its crop response was still no more than 77%. All the PAPR treatments were lower than Treatment MCP (monocalcium phosphate) in yield.

Table 10-8 Crop responses to PAPRs on 2 red soils (3 harvests, ryegrass, pot experiments)

Treatment	Red soil from Jiangxi				Red soil from Yunnan			
	Yield (g/pot)	%	P uptake (mg/pot)	%	Yield (g/pot)	%	P uptake (mg/pot)	%
NK	Nil	-	-	-	13.13f	55	15.4f	22
MCP	21.89a	100	60.9	100	23.9a	100	71.2a	100
S30K	16.4d	75	37.0d	61	22.8a	95	40.8b	58
S60K	18.0d	82	40.0a	66	24.9a	104	62.1a	97
C1K	18.7d	85	43.7c	72	22.2a	93	44.1d	62

Note: the P application rate was 120 mg/kg for every treatment with P addition.

Table 10-9 Crop responses to PAPR on red soil from Jinhua of Zhejiang province (pot experiment in France, with Agrostis as test plant)

Treatment	Weight (dry matter)		P uptake	
	mg/pot	%	mg/pot	%
NK	79a	37	0.13a	34
TSP	215.9b	100	0.38c	100
RPK	120.9ab	56	0.22b	58
S30K	178.8b	83	0.39c	102
SN30K	203.9b	94	0.36c	95
C1K	368.6d	170	0.48d	126
SPJ	68.0a	31	0.12a	32
S-30J	81.4	38	0.16a	42
SN-30J	256.4c	122	0.23b	60
C1J	242.3c	112	0.28c	74

*: K stands for Kunyang, J for Jinning, please refer to the end of the chapter for other codes.

Table 10-10 Available P (mg/kg) added into the soil with fertilizer

Treatment	Water soluble P	Citrate soluble P
RP	1.2	-
MCP	-	-
S30K	26	53
S60K	34	83
SP60K	80	86
C1K	36	62

Table 10-11 Yield of ryegrass in relation to acidulation degree of PAPR and number of harvests (red soil from Jiangxi, phosphate rocks from Kunyang)

Treatment	1st harvest		6th harvest	
	Dry weight (g/pot)	%	Dry weight (g/pot)	%
NK	0.22f	5	0.63d	2
RP	0.80e	17	22.7c	75
MCP	4.76a	100	30.2a	100
S30	2.20d	46	22.4c	74
S60	3.66bc	77	26.6b	88
SP60	4.06b	84	28.6a	95
C1	3.11c	45	26.7	88

The situation, however, was different with the red soil from Yunnan (Table 10 – 8). No matter how the acidulation degree of PAPR varied, the crop changed a little in yield, not significantly in statistics. The situation with the red soil from Zhejiang appeared to be in the middle of that of Jiangxi and Yunnan (Table 10 – 9).

10.4.2. Soil P fixation capacity and relative crop response

The red soils used in this experiment varied sharply in soil P fixation capacity (Table 10 – 12).

Table 10-12 P fixation capacity of red soils for test (mg/kg soil)

Location	Crop for test	Fixation capacity
Yingtan, Jiangxi	Ryegrass (pot)	364.1
Qujing, Yunnan	Ryegrass (pot)	247.7
Jinhua, Zhejiang	Ryegrass (pot)	311.9
Yingtan, Jiangxi	Peanut	356.5
Jinxian, Jiangxi	Sesame	95.0
Jiujiang, Jiangxi	Sesame	178.0

Location	Crop for test	Fixation capacity
Shanggao, Jiangxi	Soybean	283.5
Shanggao, Jiangxi	Sweet potato	252.8
Jinhua, Zhejiang	Soybean	246.0
Kaihua, Zhejiang	Soybean	227.5
Jinhua, Zhejiang	Soybean	195.7
Jinhua, Zhejiang	Corn	346.5
Ningxiang, Hunan	Mung bean	317.5

General speaking, soil P fixation is good for PAPR to display its effectiveness. This viewpoint will be addressed specifically in Chapter 14 of this book. Based on the results of our experiments, P fixation capacities of the soils can be sorted into 3 grades, high, medium and low. P fixation capacity > 300 mg/kg is "high", between 100 ~ 300 mg/kg "medium" and < 100 mg/kg "low". Of course, this is only based on results obtained with one specific method. Different methods would yield widely different results. The data in Table 10 – 12 are results obtained with a method introduced in a book edited by Lu Rukun (1999). It is clearly shown in the Table 10 – 12 that the 3 soils in the pot experiment are different in P fixation capacity.

- The fixation capacity of the soil from Yingtan of Jiangxi was 364.1 mg/kg;
- The fixation capacity of the soil from Jinhua of Zhejiang was 311.9 mg/kg;
- The fixation capacity of the soil from Qujing of Yunnan was 247.7 mg/kg。

Their differences in P fixation capacity led to differences in crop response to PAPR in the pot experiment. On the red soil from Jiangxi, with the highest P fixation capacity, PAPR of S60K has only

82% in relative crop response (Table 10 – 8) and only 77% in the first harvest (10 – 11) while on the red soil from Qujing of Yunnan, crop response to PAPR of S30K reached as high as 95% (Table 10 – 8). One of the major causes is probably that the soil is the category of “medium” in P fixation capacity. On the soil in Jinhua of Zhejiang, crop response lay in between those on the other two soils. Crop response to PAPR of S30K was only 83% that to TSP (95% on the soil from Yunnan). It is, therefore, quite clear that soil P fixation capacity affects crop response to PAPR variedly, and that it is unwise to hold that the effect of soil P fixation capacity on crop response to PAPR is always the same. Based on the findings of the experiment, it can be held that soils medium in P fixation capacity PAPR may show best of its effectiveness. But on soils high in P fixation capacity, effectiveness of PAPR is affected because a large amount of water soluble P is still fixed. Experiments also indicated (Table 10 – 13) that on the red soil from Yingtan of Jiangxi, high in P fixation capacity, the recovery rate of resin P was only 4% (70 mg/kg P added) and that of Olsen P only 12%, while on neutral paddy soils and calcareous fluvio-aquic soils, the recovery rate was 30% and 50%, respectively.

Table 10-13 Soil P fixation capacity and recovery rate of P fertilizer

	Red soil (Jiangxi)	Paddy soil (Jiangsu)	Fluvio-aquic soil (Henan)
Soil fixation capacity (mg/kg)	364	177	85
Recovery rate*(%)			
70 mg/kg added	3.4	34.6	73.3
100 mg/kg added	7.6	39.3	82.6
Olsen P recovery rate (%)			
70 mg/kg added	12	30	50
100 mg/kg added	16	32	53

*: P recovered by resin

In order to improve effectiveness of PAPR on soils high in P fixation capacity, tests on effect of granulating PAPR on crop response were carried out. When PAPR is prepared into granules, its contact area with soil gets less, thus reducing fixation of fertilizer P by soils (Table 10 – 14). The table clearly shows that when PAPR of S60K was granulated, its relative crop response rose up to 107%, that is to say, exceeding MCP's. Obviously on soils high in P fixation capacity, it is of great significance to reduce P fixation. The simplest way to do is granulate the fertilizer. So when PAPR is applied to soils high in P fixation capacity(364.1mg/kg), the fertilizer ought to be granulated. On soils medium in P fixation capacity(247.7mg/kg), like the red soil from Qujing of Yunnan, granulation did not show its effect (Table 10 – 14), indicating that it is not necessary to stress the need for granulating the fertilizer on soils medium in P fixation capacity.

Table 10-14 Effect of granulation of PAPR on crop response in soil different in P fixation capacity

Treatment	Red soil (Jiangxi)		Red soil (Yunnan)	
	g/pot	%	g/pot	%
NK	Nil	-	13.1f	54
MCP	22.0a	100	24.0a	100
S60K	18.1c	80	24.9a	104
S60KG*	23.6a	107	24.8a	104

*: Here G stands for granule.

10.4.3. Soil acidity and residual effect

Soil acidity is also a main soil property that affects residual effect of PAPR. On acidic red soils (pH 4.5) from Jiangxi, its effect is particularly obvious. The relative effectiveness (residual effect) of the PAPR rose steadily with the time (Table 10 – 11).

- The relative effectiveness of S30 rose from 46% to 74%;
- The relative effectiveness of S60 rose from 77% to 88%;
- The relative effectiveness of SP60 rose from 84% to 95%;
- The relative effectiveness of C1 rose from 65% to 88%.

With the time goes on, the relative effectiveness of PAPR against that of fully acidulated fertilizer rises because the portion of phosphate rocks that have not been reacted in the PAPR continue to be dissolved, releasing some additional available P. this dissolution process depends mainly on soil acidity, and of course is also contributed by the interaction between the two major portions of PAPR, soluble P and unreacted phosphate rocks.

10.5 Effectiveness of PAPR on different crops

In this experiment, a total of 10 species of crops were tested. Table 10 – 15, 10 – 16 and 10 – 17 show crop responses from peanut, corn and sesame to PAPR. It is indicated in the tables that the crop responses from corn and sesame were higher than that from peanut. For instance, the mean relative effectiveness of PAPRs on peanut was 88%, on corn 107% and on sesame 92%. The three crops, however, did not grow on the same soil. Besides the crops, soils are also an important factor influencing crop yield. So it is hard to judge effect of crops on effectiveness of PAPR. The results of the experiment demonstrated that even if there were any difference, it was not big.

Table 10-15 Crop response from peanut (red soil from Yingtan of Jiangxi province)

Treatment	Mean yield (kg/ha)	%
NK	1433b	78
SSP	1833a	100
SP60K	1600b	87
C1K	1667a	91
SP60J	1600b	87
C1J	1600b	87

*: Soil properties: pH (H_2O) 4.5, Olsen P: 4.8 mg/kg, P fixation capacity: 356 mg/kg, TN%: 010.

Table 10-16 Crop response from corn (red soil from Jinhua of Zhejiang province)

Treatment	Mean yield (kg/ha)	%
NK	4330d	85
SSP	5075be	100
SP60K	5480a	108
C1K	5350ab	105
SP60J	5605b	110
C1J	5280b	104

*: For soil properties, please refer to Table 10 – 4.

Table 10-17 Crop response from sesame (red soil from Jiujiang of Jiangxi province)

Treatment	Mean yield (kg/ha)	%
NK	1030c	57
SSP	1805a	100
SP60K	1605b	89
C1K	1705a	94
SP60J	1600b	89
C1J	1750a	97

*: For soil properties, please refer to Table 10 – 4.

10.6 Impact of grade of phosphate rock from Haikou on effectiveness of PAPR

The effectiveness of PAPR from Haikou rock is already summed up in Table 10 – 6. in the experiment, two kinds of Haikou phosphate rocks different in grade were used, one high and the other low. The purpose of the selection was to determine the effect of total P content in the rocks on effectiveness of the PAPR thereof. Preparation of and P contents in the PAPRs from the rocks were listed in Tables 9 – 9 and 9- 10.

Field experiments of the PAPRs were laid out and conducted in Jiangxi, Zhejiang, Jiangsu and Henan province on six crops (Table 10 – 3).

Table 10-18 Crop response to PAPR from Haikou phosphate rocks low in grade (red soils from Lanxi of Zhejiang province, soybean)

Treatment	Mean yield (kg/ha)	%
NK	1368B	93
PR	1394B	95
SSP	1475A	100
L45H	1465A	99
L75H	1500A	102
LC33H	1469A	99

Note: Soil properties: pH (H_2O) 5.0, Olsen P: 5 mg/kg, *: L stands for low in grade, H after figures for Haikou and the figures in between letters for acidulation degree

Table 10-19 Crop response to PAPR from Haikou phosphate rocks low in grade (red soils from Shanggao of Jiangxi province, peanut)

Treatment	Mean yield (kg/ha)	%
NK	3100b	86
PR	3500a	97
SSP	3600a	100
L45H	3300a	92
L75H	3200a	89
LC33H	3400a	94

Note: Soil properties: pH (H_2O) 5.5, available P: 4.8 mg/kg,

Table 10-20 Crop response to PAPR from Haikou phosphate rocks high in grade (red soils from Jinxian of Jiangxi province, peanut)

Treatment	Mean yield (kg/ha)	%
NK	1840c	66
PR	2480b	89
SSP	2800a	100
H45H	2680a	96
H75H	2720a	97
HC33H	1500b	90

Note: Soil properties: pH (H_2O) 4.9, available P: 1.0 mg/kg, *: The first letter H stands for high in grade, the letter H after figures for Haikou.

PAPRs from of rocks low in grade met with fairly good crop response from soybean and peanut in Lanxi of Zhejiang, their relative mean effectiveness reached 100% (Table 10 – 18), which means that PAPRs of every kind were equal to SSP in effectiveness. And in Shanggao of Jiangxi, its relative mean effectiveness reached 92% (Table 10 – 19). Though it is a bit lower than that in Lanxi, they pose no difference in statistics.

PAPRs from Haikou rocks high in grade received high crop response (Table 10 – 20). They stood side by side with SSP were at the same level (no difference in statistics). Therefore, it can be inferred that grade of the rocks from Haikou does not affect demonstrate the conclusion out of the above-described typical experiments that is, PAPRs from Haikou phosphate rocks, though different in grade show no difference in effectiveness.(Table 10-21)

It is noteworthy that raw phosphate rock powder from Haikou enjoyed good crop response on acid soils. Particularly rocks low in grade.

Table 10-21 Effectiveness of PAPRs from phosphate rocks different in grade from Haikou (mean of 10 experiments)

PAPR	Relative effectiveness (% against SSP)
Rocks low in grade	
L45	98
L75	101
LC	98
Mean	99
Rocks high in grade	
H45	98
H75	119
HC	94
Mean	104
Mean in total	101

The reasons why the relative effectiveness of the rocks low in grade are higher are, firstly, that they are higher in content of citrate soluble P than the rocks high in grade and, secondly, that they were tested on soils different in pH. The soil for testing the rocks low in grade was slightly more acidic (pH 4.5 ~ 5.5) than the acidity of the soil for testing the rocks high in grade was pH 4.7 ~ 6.1.

All the results demonstrate that soil acidity helps dissolved phosphate rocks from Haikou and of course the residual rocks in PAPR, too. This may explain why PAPR from Haikou rocks may have good crop response regardless of their difference in grade.

10.7 Residual effect of PAPR

10.7.1. Residual effect on acid soils

The results of the pot experiments (Table 10 – 11) show that the residual effect of PAPR lasts long and significantly, too. This is mainly because unreacted phosphate rocks in PAPR gradually dissolve under the action of soil acid, releasing available P. Therefore, its residual effect is more apparent on acid soils. Table 10 – 22 shows residual effect of PAPR from Kunyang phosphate rocks in the field experiments on acid red soils in Jiangxi. It is clearly shown in Table 10 – 22 that relative effectiveness of the residual effect of PAPR rose from 89% ~ 97% to 110% ~ 115% and from 92% to 113% in mean value. The increase is significant. On the red soils from Yingtan of Jiangxi high in P fixation capacity, residual effect of PAPR also increased (Table 10 – 23) but by a less margin than on the soil indicated in Table 10 – 21. it rose from 89% to 93% in mean value. This is because the P fixation capacity of this type of soil may be too high.

In Table 10 – 24 are listed mean results of four experiments on residual effect. Residual effect of the PAPRs ranged from 99% to 106% and averaged 103%, and was higher than the relative effectiveness on the current crops that received PAPR. It can be held that on acid soils residual effect of PAPR commonly rose as compared with their relative effectiveness on current crops.

10.7.2. Residual effect on soil different in acidity

In Table 10 – 25 are listed residual effect of PAPR on three soils different in pH. Among them red soil was 5.0, paddy soil 5.8 and fluvio-aquic soil 8.5. the table clearly shows that the residual effects of all kinds of PAPR were significant on red soil, rising from 90% to 106% on average, but dropped instead of rising on paddy soil and fluvio-aquic soil. For instance, the mean relative effectiveness of PAPRs dropped from 106% down to 85% on paddy soil and from 96% to 82% on fluvio-aquic soil.

Table 10-22 Residual effect of PAPR (in Jiujiang of Jiangxi, red soil)

Treatment	Sesame (1st cropping)		Rapeseed (2nd cropping)	
	Yield (kg/ha)	%	Yield (kg/ha)	%
NK	1030c	57	980e	89
SSP	1805a	100	1105e	100
SP60K	1605b	89	1270a	115
C1K	1705c	94	1220a	110
SP60J	1600b	89	1275a	115
C1J	1750c	97	230a	111
Mean	-	92	-	113

Note: for soil properties please refer to Table 10 – 4.

Table 10-23 Residual effect of PAPR (in Yingtan of Jiangxi, red soil, relative effectiveness %)

Treatment	Peanut (1st cropping)	Buckwheat (2nd cropping)
NK	78	75
SSP	100	100
SP60K	87	92
C1K	91	92
SP60J	87	99
C1J	89	87
Mean	89	93

Table 10-24 Residual effect of PAPR in field experiments (mean of four field experiments)

Treatment	Mean of the 1st crop	Residual effect (%)	
		Range	Mean
SSP	100	100	100
SP60K	93	100 ~ 115	105
C1K	94	96 ~ 110	104
SP60J	96	85 ~ 115	99
C1J	95	86 ~ 116	109

It is generally held that the residual effect comes from continued dissolution of unreacted phosphate rocks in the PAPR. The continued dissolution, however, needs a fundamental condition, which is acidity of the soil, or the unreacted rocks will not be dissolved. Interaction between the two major components of PAPR may help dissolve some without the aid of soil acidity, but the amount is limited. It is also shown clearly in Table 10 – 25 that without the aid of soil acidity, residual effect (% of relative effectiveness) of PAPR drops by a large margin, which at least indicates that the amount of P released from unreacted phosphate rocks in PAPR is limited. So this leads to significant decrease in residual effect in weakly acid paddy soil and calcareous fluvio-aquic soil. Treatment RPK in Table 10 – 25 is another proof. In treatment RPK, only powder out of phosphate rocks from Kunyang was applied. On acid soil its relative effectiveness with the first crop was16.8%, but its residual effect with the 2nd ~ 6th crops increased up to 86%. The increase is extremely significant in statistics, which demonstrates that the phosphate rock powder from Kunyang was dissolved fairly well in red soil from Jiangxi. Treatment RPK on paddy soil and fluvio-aquic soil did not show any substantial increase in residual effect, which is another proof that in these two types of soil unreacted phosphate rocks in PAPR were rarely further dissolved. Of course, the two soils are also different from each other. For instance, in weakly acid paddy soil, when only phosphate rock powder was applied, its relative effectiveness (including residual effect) reached 55% ~ 60%, which indicates that phosphate rock powder from Kunyang might be dissolved. The slight increase in residual effect may demonstrate some, though limited, extent of dissolution, in fluvio-aquic soil, the application of phosphate alone showed only 14% in relative effectiveness and 15% in residual effect. It may be inferred that the powder did not dissolve in such soils. Such a significant relationship between residual effect of PAPR and soil pH indicates that in calcareous soils, effectiveness of PAPR depends mainly on the portion of soluble P and that only in acid and weakly acid soils can further dissolution of residual phosphate rocks in PAPR be expected.

Table 10-25 Residual effect (% of relative effectiveness) of PAPR in different soils (pot experiment, ryegrass)

Treatment	Red soil (5.0)		Paddy soil (5.8)		Fluvio-aquic soil (8.5)	
	1st crop	2nd ~ 6th crop	1st crop	2nd ~ 6th crop	1st crop	2nd ~ 6th crop
RPK	16.8	86	55	60	14	15
MCP	100	100	100	100	100	100
S30K	46	80	92	69	85	65
S60K	78	90	106	92	402	86
SP60K	85	95	111	99	97	97
C1K	65	93	113	80	100	81
Mean (%)	69	90	106	85	96	82

Note: For soil properties, please refer to Tables 9 – 13 and 9 – 16 in Chapter 9; the mean does not include Treatment RPK; the figures in the parentheses after soils are pH values.

10.8 Evaluation of effect of unreacted phosphate rocks in PAPR (residual phosphate rocks); A new concept: theoretical available P of PAPR

From the preceding paragraph (10.7), it is known that on acid and weakly acid soils the yield-increasing effect of PAPR is attributed not only to the portion of soluble P, but also to the unreacted portion of residual rock in the fertilizer. As of yet, however, there seems to be no objective evaluation method. Consequently, a new concept is put forth here, i.e. theoretical available P of PAPR.

It is known that all the P in monocalcium phosphate is in the available form or water-soluble form. But when it is applied into soil only a portion of the P is really absorbed by crops as is demonstrated by large numbers of experiments. Therefore, if P absorbed by a plant and the proportion of water soluble P applied in a given soil are known, it is feasible to calculate out how much available (equivalent to water soluble) P existing in the soil. This amount of P is termed as “theoretical available P”. this concept makes it possible to evaluate the contribution of the two portions of P, soluble P and rock P, in PAPR. If the theoretical available P is higher than the amount of soluble P in the PAPR applied, it means that the unreacted phosphate rocks in PAPR may contribute some available P.

The use of the concept of theoretical available P makes if possible to figure out how much available P in any P fertilizer actually contributes to yield of the crop and how much adverse effect of soil P fixation on available P.

Table 10 – 26 shows that in acid soils, the theoretically

available P of the phosphate rock powder from Kunyang is far greater than that of soluble P and that of 2% citrate soluble P as well, which indicates that in acid soils phosphate rock powder dissolves so well that its theoretical available P reaches one half of the total P in the powder added.

Table 10 – 26 also shows that the theoretical amounts of available P of the PAPR in the test are all similar to those of 2% citrate soluble P, respectively, forming a ratio of 1.14:1, which indicates that 2% citric acid method can be used as a standard method for measuring available P in PAPR applied in acid soil.

Table 10-26 Theoretical available P of PAPRs in acid soil (mg/pot)

Fertilizer	P uptake	P applied			Theoretical available P
		Total P	Water Soluble P	Citric acid P	
RPK	28.2	180	0.22	41.6	92.5
MCP	55.0	180	180	-	(180)
S30K	25.7	180	28.8	61.7	84.1
S60K	34.8	180	61.2	97.2	113.9
SP60K	38.5	180	105.8	124.2	126.0
C1K	29.5	180	43.4	84.6	96.5

Note: theoretical available P (mg/pot) = crop P uptake × (P applied in Treatment MCP)/(P uptake in the same treatment) = P uptake × (proportion of water soluble P applied taken up by crop, here is 180/55)

The concept of theoretical available P can also be successfully applied to soils different in acidity (Table 10 – 27).

Table 10-27 Theoretical available P in PAPR on soils different in acidity (pot experiment)

Fertilizer	Soluble P added	Theoretical available P (mg/pot)		
		Red soil	Paddy soil	Fluvio-aquic soil
RPK	0.22	92.5	38.4	1.85
MCP	180	180	180	180
S30K	28.8	84.1	51.6	42.9
S60K	61.2	113.9	101.0	77.3
SP60K	105.8	126.0	131.3	114.0
C1K	42.4	96.5	68.4	62.9

In table 10 – 27, it is clearly shown that when fertilizers equal in P were added, they differed significantly in theoretical available P on different soils as a result of the reactions between the fertilizers and the soils.

From Table 10 – 27, it can be inferred that when applied on acid red soils and weakly acid paddy soils, PAPR was higher in theoretical available P than their soluble P, when applied on fluvio-aquic soils it showed no big difference between the two, which indicates that the soluble effect of residual phosphate rocks in the PAPR was greater in acid and weakly acid soils than in calcareous soils.

Appendix: Meaning of the codes in this chapter 10:

- K = phosphate rocks from Kunyang
- J = phosphate rocks from Jinning
- H = phosphate rocks from Haikou
- S = sulfuric acid
- P = phosphoric acid
- N = nitric acid
- 30, 50 or 60 = acidulation degree (%)
- SSP = superphosphate
- TSP = tri-superphosphate
- MCP = monocalcium phosphate
- C = compound fertilizer
- RP = phosphate rocks

Chapter 11. Experiment on Paddy Soil

Paddy soil is one of the most important soils in China, spreading over an area of 2.5 million hectares or accounting for 29% of the country's total area of grain producing farmlands or 23% of the world's total paddy soil area. It plays a critical role in China's agricultural production, because the output of rice accounts for 44% of the country's total grain production and for 39% of the world's total rice output.

Paddy soils are widely distributed in the southern part of China, i.e. areas south to the geographic line from Qinling Mountains to the Huaihe River, and east to the Qinzang Plateau, and areas such as the Changjiang River Valley. About 93% of the country's paddy soils are distributed in these areas and concentrated in the middle and lower reaches of the Changjiang River, the Sichuan Basin, the Pearl River Delta and the Plains in the western part of Taiwan.

11.1 Experiments

In terms of the application of PAPR, paddy soil is different from other soils in characteristics.

When paddy soil is flooded, its pH tends toward neutral (Yu Tianren, et al. 1983), rising if it is acidic and falling if alkaline. That is to say, no matter whether it is originally acidic or alkaline (Table 11 – 1), it turns to be neutral under water. This is not good to dissolution of residual phosphate rocks in PAPR will be affected.

Flooding will increase available P content in the paddy soil to a varying extent (Lu Rukun, et al. 1998), which hence will decrease crop response to PAPR. It is, therefore, of particular significance to study crop response to PAPR on paddy soils.

Table 11-1 Variation of pH in paddy soil after flooding

	Acidic paddy soil	Alkaline paddy soil
Before flooding	5.37	8.0
After flooding	6.75	6.9

During the period of 1988 ~ 1990, the Institute of Soil Science, Academia Sinica, conducted study on PAPR in cooperation with IRRI (International Rice Research Institute in the Philippines). The PAPR used in the experiment was prepared out of phosphate rocks from Morocco with two acidulation degrees, 15% and 30%. The properties of the PAPRs are listed in Table 11 – 2. IRRI supplied both the phosphate rocks and the PAPRs.

Field experiments were mainly carried out in Jiangxi and Jiangsu provinces. In Table 11 – 3 are listed properties of the soils for test.

Beside, the Institute of Soil Science, Academia Sinica, also has some field experiments carried out in cooperation with the Guangdong Soil Institute.

Table 11-2 Properties of PAPRs and phosphate rocks for test (P_2O_5, %)

Fertilizer	Total P	2% citric acid soluble P	Water soluble P
S15M	28.2	8.7	2.2
S30M	27.4	12.9	1.7
RPM	33.2	9.2	Trace

Note: S stands for acidulation with sulfuric acid, the figure in between two letters for acidulation degree, M for Morocco and RP for phosphate rocks.

Table 11-3 Properties of the soils for test

Item	Paddy soil (red soil)* (Yingtan, Jiangxi)	Paddy soil (yellow brown earth*) (Liyang, Jiangsu)
pH (H_2O)	5.1	5.8
Organic matter (%)	2.85	1.7
Total P (P %)	0.036	0.031
Olsen P (mg/kg)	3.2	5.5
Exchangeable K (mg/kg)	64	57.0

*parent soil

In Yingtan of Jiangxi, the field experiment was under a rotation system of early rice, late rice and peanut and in Liyang of Jiangsu of rice and rapeseed. In the field experiments, only the first crop received PAPR and the following crop or crops were used to test residual effect of the PAPR.

The application rate for P fertilizers was 30 kg/ha·P and for N and K fertilizers according to the local recommendation.

The field experiments had five treatment and three replicates:

- Treatment 1:NK (without P);
- Treatment 2: TSP;
- Treatment 3: S15M;
- Treatment 4: S30M;
- Treatment 5: RPM

The acreage of each plot was 15 m^2.

Besides the above-described experiments, field experiments on paddy soils conducted in cooperation with CIRAD are also included in this chapter.

11.2 Results

11.2.1. Crop response on acidic paddy soils

Table 11 – 4 shows crop responses to PAPRs on two different types of acidic paddy soils in Jiangxi and

Guangdong, respectively.

Table 11-4 Response of rice to PAPRs on acidic paddy soils

Treatment	Yingtan, Jiangxi		Fanyu, Guangdong	
	Yield (kg/ha)	%	Yield (kg/ha)	%
NK	5533d	84	5457c	90
TSP	6600a	100	6049a	100
S15M	5933c	90	6315a	104
S30M	6267b	95	6692a	111
RPM	5600d	85	-	-

Note: The paddy soil in Guangdong is acid sulfatic soil with pH at 4.3 and Olsen P at 5.2 mg.kg

It is clearly shown that the crop responded quite well to PAPR on the two soils. In Jiangxi when PAPR was acidulated to 15%, the crop response to PAPR was lower than to TSP and when to 30%, it reached 95% of that to TSP. But no crop response was observed to RPM, which is believed to be a reflection of the rise in pH as a result of flooding. In this case, even phosphate rocks like those from Morocco with high reactivity will hardly play a yield-increasing role.

In Guangdong, the paddy soil was a strongly acidic sul phate soil (pH 4.3). on such a soil when the PAPR was acidulated to 15%, the crop response to PAPR reached or exceeded that to TSP and when to 30%, it was even more significant.

Results of another two experiments conducted in Yujiang of Jiangxi are listed in Tables 11 – 5 and 11 – 6. The data in Table 11 – 5 show that S15M had little crop response and S30M some.

Table 11-5 Crop responses to PAPRs on paddy soil derived from the Tertiary Red Soil (early rice, in Yujiang of Jiangxi)

Treatment	Yield (kg/ha)	%
NK	4500b	89
TSP	5033a	100
S15M	4567b	91
S30M	4667b	93

Note: Soil pH 5.5 and Olsen P 4.2 mg/kg.

Table 11-6 Crop responses to PAPRs on paddy soil derived from the Quaternary Red Clay (early rice, in Yujiang of Jiangxi)

Treatment	Yield (kg/ha)	%
NK	4782d	85
TSP	5645a	100
S15M	5127c	91
S30M	5348b	95
RPM	4812d	85

Note: Soil pH (H_2O) 5.1 and Olsen P 3.2 mg/kg.

On paddy soils derived form the quaternary red clay S30M met with good crop response but phosphate rocks from Morocco (RPM) did little.

From the above-described results, it can be inferred that on paddy soils no crop response can be expected to phosphate rocks with high reactivity and that only when PAPR is acidulated to 30%, its crop response may reach 93% ~ 95% that to TSP. Strongly acidic soils (the acid Sulfatic soil) are exceptions.

11.2.2. Crop response on weakly acidic paddy soil

In table 11 – 7 are listed crop responses from rapeseed to PAPR on weakly acidic paddy soils (pH 5.8) in Liyang of Jiangsu. It is clearly shown in the table that the crop yielded little when no P was applied and that RPM had some crop response. The table also shows that the crop responses to PAPR were higher than that RPM, but much lower than that to TSP. When PAPR was 15% in acidulation degree, its relative yield was only 61% and when 30% it rose up to 72%. Therefore, it can be inferred that on weakly acidic paddy soils, even for rapeseed, 30% in acidulation degree is not enough for PAPR even out of phosphate rocks from Morocco. No residual effect was observed on rice for the second crop.

On weakly acidic paddy soils, two other features ought to be taken into account when PAPR is used, i.e. one is that the soils are not acidic enough to bring residual phosphate rocks in the PAPR into play and the other is that in comparison with acidic red soils, they are a bit lower in P fixation capacity (Table 10 – 12 in Chapter 10), which leads to better crop response than on acidic red soils when PAPR is acidulated to a certain degree and applied at the same rate (in terms of available P). when PAPR is applied to a weakly acidic paddy soil low in P fixation capacity, on one hand its low acidity fails to turn residual phosphate rocks in the PAPR into available P and on the other hand less available P in PAPR is fixed by the soil. The contradictory factors jointly determine effectiveness of PAPR on weakly acidic paddy soils.

Table 11-7 Crop response and residual effect of PAPR on paddy soils in Jiangsu

Treatment	First crop (rapeseed)		Second crop (rice)
	Yield (kg/ha)	%	Yield (kg/ha)
NK	Failed	-	6333a
TSP	1200a	100	5733a
S15M	133c	61	6067a
S30M	867b	72	6200a
RPM	667c	56	5667a

Note: Soil pH 5.8 and Olsen P 1.9 mg/kg.

In order to make it clearer, in Table 11 – 8 are listed results of the experiments on red soil in Jiangxi and paddy soil in Jiangsu. The table shows clearly that the theoretical available P that RPK provides is only 38.4 mg/pot (Cf Paragraph 10.8, Chapter 10), indicating that the solubility of RPK is much lower in paddy soil than in acidic red soil. Table 11 – 8 reveals, however, the recovery rate of P of most types of PAPR is higher in paddy soil than in acidic red soil, which demonstrates that on paddy soil, lower P fixation capacity leaves more available P available. There are a few exceptions that the recovery rate of P being lower in paddy soil than in red soils. These might be due to a larger proportion of residual phosphate rocks and a resultant smaller proportion of available P in some PAPR. For instance, with S30K and C1K, the good effect of "low P fixation capacity" is not great enough to counteract the bad effect of "low solubility of unreacted part", which also indicates that the effectiveness of PAPR is determined by which of the above two contradictory factors is stronger.

Table 11-8 P availability of PAPR on red soil and paddy soil

Treatment	P recovery rate (%)		Theoretical available P(mg/pot)	
	Red soil	Paddy soil	Red soil	Paddy soil
RPK	15.7	8.9	92.5	38.4
MCP	31.0	41.7	180.0	180.0
S30K	14.3	12.0	84.1	51.6
S60K	19.3	23.4	113.9	101.0
SP60K	21.4	30.4	126.0	131.3
C1K	16.4	15.8	96.5	68.4

Note: Red soil with pH 5.0 and Olsen P 1.0 mg/kg ; paddy soil with pH 5.9 and Olsen P 1.9 mg/kg.

11.2.3. Residual effect of PAPR on paddy soil

a Acidic paddy soil

First of all, let us look at residual effect of PAPR on acidic paddy soil. Table 11 – 4 shows responses from the first crop in the experiment on acidic paddy soil derived from red soil in Jiangxi. Responses from the second and third crops are listed in Tables 11 – 9 and 11 –10.

The Table 11 – 9 shows that the residual effect was very limited on the second crop, late rice, but significant on the third upland crop (Table 11 – 10). The mean relative effectiveness of the three types of fertilizers (two types of PAPR and RP)was 90% on the first crop, 100% on the second but with the main yield increasing rate being only 8%, and 107% on the third crop with the mean yield increasing rate being 24%.

Table 11-9 Residual effect of PAPR on acidic paddy soil (late rice, second crop, Yingtan of Jiangxi)

Treatment	Yield (kg/ha)	%
NK	5200	92
TSP	5667	100
S15M	5667	100
S30M	5467	96
RPM	5867	104

Table 11-10 Residual effect of PAPR on acidic paddy soil (peanut, third crop, Yingtan of Jiangxi)

Treatment	Yield (kg/ha)	%
NK	999b	83
TSP	1200a	100
S15M	1333a	111
S30M	1333a	111
RPM	1200a	100

On strong acid soils (acid Sulfatic soil) in Fanyu of Guangdong, some residual effect of PAPR was observed (Table 11 – 11). The relative effectiveness of PAPR on the first crop was 107% (Table 11 – 4) and the residual effect only 103%..

On acidic paddy soil, residual effect on upland crops was significant. This situation is due to phosphate rocks used with high reactivity (e.g. Morocco rocks) to produce PAPR. But residual effect on late rice was not good, and what is more, even the powder of highly active Moroccan phosphate rocks per se did not show a significant effectiveness.

Table 11-11 Residual effect of PAPR (late rice, second crop) (Fanyu of Guangdong, paddy soil)

Treatment	Yield (kg/ha)	%
NK	4483.5c	88
S15M	5079b	100
S30M	5241.5b	106
TSP	5602.5b	100

b Residual effect on weakly acidic paddy soil

In Table 11 – 12 are listed effectiveness and residual effect of PAPRs out of phosphate rocks from Haikou.

It is shown clearly that all the three types of PAPR out of phosphate rocks from Haikou, including C75H, whose acidulation degree was as high as 75% failed to reach 90% in relative effectiveness of corn, the first crop. This indicates that on weakly acidic paddy soil, PAPR out of phosphate rocks with low reactivity was also lower (statistically significant) than SSP (fully acidulated fertilizer) in effectiveness on upland crop, but showed fairly high residual effect, which reached up to the level of SSP, except in the case of C75H.

Table 11-12 Effectiveness and residual effect of PAPRs from Haikou phosphate rocks on paddy soil (pH 6.1, AV.P 3.5mg/kg corn-forage corn, Jurong of Jiangsu)

Treatment	Corn, first crop		Forage corn, second crop	
	Yield (kg/ha)	%	Yield (kg/ha)	%
NK	4450d	62	2200	62
RPH	4850d	67	2500	70
SSP	7200a	100	3550	100
SP45H	6100a	85	3450	97
SP75H	6200b	86	3750	106
C75H	5900b	82	3050	86

11.3 Conclusions

In this chapter four factors that may affect effectiveness of PAPR are discussed, i.e. soil acidity, soil P fixation capacity, reactivity of phosphate rocks and acidulation degree of PAPR.

On paddy soil effectiveness of PAPR depends to a large extent on interactions of the above-listed four factors. Experiments indicate that on strongly acidic paddy soils, such as acid Sulfatic soil, similar crop responses could be observed from rice to fully acidulated fertilizers of PAPR, even at lower acidulation degree, if the phosphate rocks are of high reactivity (like Morocco rocks). This is, however, only a rare case. Generally, on paddy soils grown with rice in South China, PAPR with acidulation (H_2SO_4) degree of 60% or more should be applied. Even if so, its residual effect on successive rice crops will not necessarily be significant.

On acidic paddy soils grown with upland crops, PAPR will not only show significant crop response, but also fairly high residual effect.

On common paddy soils, it is hard to dissolve phosphate rocks including those with high reactivity. When the field is cultivated alternately with upland crops following paddy rice, significant residual effect can be observed.

On neutral paddy soils, PAPR usually falls below fully acidulated P fertilizer in effectiveness if the product is prepared out of phosphate rocks with low reactivity (e.g. rocks from Haikou), except when the product is highly acidulated.

Chapter 12. Effectiveness of PAPR on Calcareous Soils

12.1 Experiment conditions

In order to learn how crops respond to PAPR on calcareous soils, pot experiments were conducted.

The soil used in the experiment was fluvio-aquic soil distributed widely in the North China Plain and gathered from Fengqiu County of Henan Province. Its basic properties are listed in Table 12 – 1.

Table 12-1 Basic properties of fluvio-aquic soil for test

Properties	%	Properties	Unit
Clay	28.3	pH (H_2O)	8.45
Silt	57.8	CEC	14.7 cmol/kg
Sand	13.6	$CaCO_3$	6.1%
Organic matter	1.14	Olsen P	3.45 mg/kg
Total N	0.08	Total P	0.065%

The pot experiment was designed to have 7 treatments and 4 replicates, that is, 1) CK with no P applied; 2) phosphate rock powder from Jinning of Yunnan < 100 μm; 3) MCP; 4) S30; 5) S60; 6) SP60 and 7) C1. Properties of the PAPRs used in the pot experiment are listed in Table 12 – 2.

Table 12-2 Properties of PAPRs in the pot experiment

PAPR*	Acid for acidulation	Acidulation degree (%)	Total P (P_2O_5) (%)	% of total P	
				Water Soluble P	2% CAP**
RP		0	20.4		23.1
S30	H_2SO_4	30	19.1	16.0	34.3
S60	H_2SO_4	60	16.9	34.0	54.1
SP60	H_2SO_4+ H_3PO_4	60	28.4	58.8	69.0
C1	H_2SO_4+ MAP	30	24.2	29.7	47.6

*: Please refer to the meaning of the codes at the end of Chapter 10.

**: CAP denotes citric acid soluble P

Each pot contained 1.5 kg of soil applied with 180mg of P, 0.23g of N (urea) and 0.19g of K (K_2SO_4). In each pot 20 ryegrass seeds were sown in November. The first harvest of ryegrass was conducted in January the next year and followed by three harvests with an interval of 6 weeks in between each harvest. Then the grass failed to survive the hot summer of that year. Seeds were sown again in the fall and then two more harvests were carried out, making the number of harvests to 6. After each harvest, NK was applied at the same rate as for the first time, but no P any longer.

The harvested plants were oven-dried and analyzed for P content. Soil samples were collected after the first and second sowing and the last harvest for analysis of P forms with the method designed by Jiang, et al. (Jiang et al., 1989).

12.2 Crop yield in different treatments

Yields of the crop in the pot experiment are listed in Table 12 – 3.

Table 12-3 Yields of the crop in different treatment (g/pot)

Treatment	CK	RP	MCP	S30	S60	SP60	C1
1st sowing							
1st harvest	0.75c	0.88c	6.38a	5.45b	6.51a	6.20a	6.42a
2nd harvest	1.62d	1.58d	9.18a	7.69a	8.71a	9.21a	8.54a
3rd harvest	1.14a	1.20d	11.83a	6.93c	9.89b	11.30a	9.94b
4th harvest	0.93e	1.18e	5.26a	2.38d	3.87c	4.73b	2.67a
Subtotal	4.57f	4.97f	33.21a	22.83e	29.55c	32.06c	28.10d
2nd sowing							
1st harvest	0.52e	0.54e	6.05a	2.29d	4.27b	4.55b	3.15c
2nd harvest	3.21e	3.37e	9.00a	4.70d	6.88b	6.18c	4.42d
Subtotal	3.73d	3.91d	15.05a	6.93c	11.15b	10.73b	7.56c
Grand total							
Dry wt.	8.91f	8.91f	48.37a	29.79e	40.75c	48.82b	35.64a
Relative %		1.5	100	53.6	81	86.1	68.2

Note: Relative % = (Dry wt – dry wt in CK)/(Dry wt in MCP – dry wt in CK) ×100.

It is clearly shown that the soil for test was so extremely deficient in P, the crop almost failed without P application in CK and that yields of the crop differed sharply from harvest to harvest and from treatment to treatment. In Treatment RP no significant crop response was observed. Among the treatments of PAPRs, treatment SP60 was the highest in yield, reaching 86.1% in relative percentage with MCP as 100, and S30 the lowest. The relative percentages in yield of PAPRs are positively correlated with their percentage of water soluble P or 2% CAP of total P but the former is expressed in logarithm. The regression equations for the two are as follows:

For log soluble P (x) $y = 59.1\,x - 16$

$$r = 0.953^{*} \quad n = 4$$

For 2% citric acid soluble P (CAP) (x) $y = 22.79 + 0.96\,x$

$$r = 0.959^{*} \quad n = 4$$

where y stands for relative percentage in yield; and x for percentage of soluble P or CAP of the total P.

Total P content in all the PAPR treatments is not significantly correlated to relative percentage in yield, with r being only 0.396.

In view of the fact that relative percentages in yield of the all the 6 harvests are significantly related to percentage of soluble P or CAP of the total P and not to total P, it can be inferred that crop response to PAPR depends mainly on content of water soluble P or CAP on calcareous soils. Therefore on such soils, PAPR, if below 100% in acidulation degree, can hardly compete with MCP, a fully acidulated fertilizer. In addition, from the fact that relative percentage in yield has nothing to do with total P of PAPR, it can be inferred that between MCP and unreacted phosphate rocks occurs no reaction that may significantly help increase content of available P.

12.3 Relative yield of each harvest

Table 12 – 4 shows relative yield of the four harvests after the first sowing.

It is clearly revealed in the table that the first harvest showed all the PAPRs, except S30, were similar to MCP in crop response, but crop responses to the PAPRs declined with increase in the number of harvest, which is different from the results of the experiment on some acid soils. This is another proof that between soluble P and unreacted phosphate rocks of PAPR occurs no reaction contributing to content of available P. In terms of relative percentage of the total yield of the four harvests (of the that of MCP), only the PAPR with soluble P accounting for 60% or more of total P was equal to MCP.

Table 12-4 Relative yield of each harvest (yield of MCP as 100)

Treatment	1st harvest	2nd harvest	3rd harvest	4th harvest	Mean
RP	2	0	1	6	1
MCP	100	100	100	100	100
S30	83	80	54	33	64
S60	102	94	82	68	87
SP60	96	100	95	88	96
C1	101	92	82	40	82

12.4 Crop P uptake in different treatments

In Table 12 – 5 listed are P uptakes by the crop in different treatments.

Table 12-5 P uptakes by the crop in different treatment (mg/pot)

Treatment	1st sowing (4 harvests total)		2nd sowing (2 harvests total)		Grand total	
	mg/pot	%	mg/pot	%	mg/pot	%
CK	3.68f	-	2.23d	-	5.87	0.06
RP	4.20f	0	2.68d	0	6.85	1.0
MCP	87.95a	100	13.33a	100	101.3	100
S30	24.05e	24	4.65c	21.8	28.6	23.8
S60	38.85c	42	6.93b	42.3	45.75	41.8
SP60	58.90b	66	7.43b	47	66.31	63.3
C1	34.50d	37	4.70c	22	39.21	34.9

Table 12 – 5 shows that crop P uptake and crop yield followed the same pattern only with the former being more significant. In terms of total P uptake (two sowings), all the PAPR treatments were lower than Treatment MCP.

But in terms of recovery rate of water soluble P in the fertilizers (Table 12 – 6), Treatment MCP was the lowest, which indicates that the crop might have absorbed some 2% citric acid soluble P. Treatment RP is another proof of some 2% citric acid soluble P being used though limited in amount. On the other hand there is also such a probability that PAPR contains some soluble P that may have some so-called “biological stimulating effect”, promoting early development of root systems.

Table 12-6 P recovery of different P fertilizers

Treatment	P added (mg/pot)		P uptake (mg/pot)			P recovery (%)	
	Water soluble P	CAP	1st sowing	2nd sowing	Total	Water soluble P	CAP
RP	-	41.4	0.52	1.45	1.97	-	5
S30	28.8	61.7	20.1	2.42	22.82	79	37
S60	61.2	97.2	35.3	4.7	40.0	65	41
SP60	106	124.2	55.2	3.3	58.5	55	47
C1	54	85.7	30.8	2.5	33.3	62	39
MCP	180	-	84.3	11.1	95.4	53	-

12.5 Forms and characteristics of P from PAPR applied to soil

12.5.1. Characteristics of P forms in soil after application of PAPR

In Table 12 – 7 listed are forms of P (inorganic P) in the soil after PAPR applied.

Table 12-7 Forms of P from PAPR applied in soil (mg/kg)

Form	Original soil	CK	RP	S30	S60	SP60	C1	MCP
Ca_2-P**	2.28							
1*		2.19	2.31	3.54	4.1	4.4	3.8	4.5
2*		2.13	2.10	2.90	3.5	3.6	2.7	4.1
Ca_8-P	31.7							
1		30.6	35.1	31.5	33.3	39.3	33.3	46.7
2		29.7	34.1	29.2	30.7	35.3	31.3	44.9
$Ca_{10}-P$	208.6							
1		206.9	264.4	264.4	241.0	225.1	254.0	206.7
2		202.8	265.9	263.7	240.3	218.0	248.7	206.7
O – P	26.7							
1		24.9	23.1	26	26.2	25.6	28.9	25.6
2		24.2	23.4	28.2	26.7	24.9	27.5	22.7
Fe – P	7.3							
1		7.1	8.1	0.9	8.8	9	10.7	11.3
2		7.8	8.4	8.3	9.6	9.8	10	10
Al – P	9.5							
1		8.8	10	7.9	13.9	11.9	10.7	14
2		8.7	11.3	7.9	10.7	11.3	11.5	10.9
Total P	285.7							
1		280.7	343	342.3	327.[illegible]	315.3	340.7	308
2		274.7	345	240.1	321.5	302.8	331.1	299

Note: *: 1 stands for data after the first sowing and 2 after the second.

**: Ca_2-P denotes the similar compounds of dicalcium phosphate; Ca_8-P ocatacalcium; $Ca_{10}-P$ apatite, Fe – P iron phosphate; Al - P aluminium phosphate.

It is shown in Table 12 – 7 that in the original soil, Ca – P accounted for 85% of the total inorganic P (among them, Ca_2-P for 0.8%, Ca_8-P for 11.1% and $Ca_{10}-P$ for 73%), Fe – P for 2.6%, Al – P for 3.3% and O – P, which is dominant in acid soils, only for 9.4%. When 180mg/pot P (120mg/pot) was added into each pot, soil total P increased.

It is discovered that the more water soluble P in the fertilizer applied, the less the increase in soil total inorganic P after the crop is harvested, which indicates that the higher the proportion of water soluble P in the fertilizer, the more P taken up by the crop. Calculation of the experiment revealed that the amount of P applied was higher than the sum of the amounts of P absorbed by the crop and remaining in the soil. The difference ranged from 6.7 to 37.6 mg/kg, which may be mainly a result of transformation of inorganic P into organic P.

Fertilizer application affects P of all forms in the soil. When PR was applied, over 70% of its P remained in the form of $Ca_{10} - P$. The 23% of P in the form of 2% citric acid soluble P in the PR per se might be transformed into other P forms.

The application of water soluble P fertilizer (monocalcium phosphate) increased $Ca_2 - P$, $Ca_8 - P$, Fe – P and Al – P, but seemingly not $Ca_{10} - P$. It used to be held that when water soluble P was applied into calcareous soil, it rapidly turned into $Ca_2 - P$ and then after a period of time into $Ca_8 - P$ (Bell et al., 1970). Bell, et al. did not actually find any further transformation into $Ca_{10} - P$, though Lehr (1958) thought that $Ca_8 - P$ might possibly transform into colloidal apatite. In this experiment, no significant increase was found in $Ca_{10} - P$, probably because the experiment did not last long enough.

Table 12 – 7 also shows that if PAPR applied is high in content of unreacted phosphate rock, the soil is correspondingly high in $Ca_{10} - P$, forming a linear regressive relationship with $r = 0.972^{**}$ reaching significance at 1% level and the slope of the straight

line being 1.19, close to 1. All these mean that almost no transformation with the unreacted PR in PAPR in calcareous soils. As was discussed in the previous paragraphs, in Treatment PR a portion of PR was transformed into various forms of P except $Ca_{10}-P$. But the unreacted PR in PAPR remained unchanged, which probably indicates that the rock phosphate reduce its reactivity during production processes.

12.5.2. Bioavailability of different forms of P

In Table 12 – 8 listed are correlation coefficients between form of P in the soil and P uptake by the crop.

Table 12-8 Correlation coefficients between form of inorganic P and total P uptake by the crop

Phosphorous Form	P uptake		
	1st sowing	2nd sowing	Total P uptake
Ca_2-P	0.903**	0.903**	0.956**
Ca_8-P	0.862**	0.848*	0.794*
$Ca_{10}-P$	n.s.	n.s.	n.s.
O – P	n.s.	n.s.	n.s.
Fe – P	0.832*	0.771*	0.819*
Al – P	n.s.	n.s.	n.s.
Total inorganic P	n.s.	n.s.	n.s.

Note: * and ** stand for significance at 5% and 1% levels, respectively and n.s. for not significant

The correlation analysis (not cited) shows that the P uptake by ryegrass is significantly related to Ca_2-P, Ca_8-P and Fe – P contents in the soil, indicating the three forms of phosphate are the major forms of available P in calcareous soil though they differ sharply in character and solubility. Their correlation coefficients vary in a decreasing order of $Ca_2-P > Ca_8-P > Fe-P$.

In addition, with increase in the number of harvesting, the correlation coefficient between Ca_2-P content and

P uptake decreased and became insignificant of the fourth harvest, whereas things went the other way round with $Ca_8 - P$. The coefficient increased with the harvesting. All these demonstrate that $Ca_2 - P$ is a source of readily available P while $Ca_8 - P$ slowly available P. The former decreases steadily with the number of harvesting increase till it can not play a dominant role in P supplying.

Table 12 – 8 also shows that Fe – P is significantly related to P uptake, too. It has been demonstrated that Fe – P is similar to $Ca_8 - P$ in availability in calcareous soil (Gu, et al., 1990). The reasons why Fe – P is somewhat available to crops in calcareous soil are 1) theoretically, its solubility is assumed to be higher in calcareous soil, and 2) some exudates from the root systems of gramineous crops may help the plant absorb Fe – P from the soil (Romheld et al.. 1986; Takag, et al., 1984).

In the experiment, the correlation between Al – P and P uptake is not significant, though Al – P has been proved fully available (Gu Yichu, et al., 1990). The insignificant correlationship here is attributed to the assumption that perhaps this so-called portion of Al – P is not really of the form of aluminum phosphate, but a mixture of Al-containing phosphate.

Analysis of the correlationship indicated that amount of water soluble P added into the soil is significantly related to contents of $Ca_2 - P$, $Ca_8 - P$ and Fe – P with coefficient being 0.932, 0.854 and 0.736, respectively. They all reached a level of extreme significance. It also showed, however, that crop P uptake and production of dry matter had nothing to do with PR in PAPR, which once again demonstrates that PR in PAPR played little role in supplying P to crops.

12.6 Discussion

Researchers in the past held that on calcareous soils PAPR might have similar crop response to what water soluble P fertilizers could get (Garbouchev, 1981; Hagin et al., 1985). They believed that hydrolysis of MCP in PPAR generated acidic saturated solution, which reacted with some unreacted PR residues. thus forming some additional soluble P. But in this experiment, nothing has been found to prove the existence of such a reaction. The reason might be that the saturated solution as a result of hydrolysis of MCP may be already neutralized by a large amount of lime and Ca ions in the soil before any reaction between the solution and PR. There is no time for the solution to dissolve any PR and hence no additional soluble P is produced, thus leaving the soluble P in PAPR to play the major role in calcareous soils. This is the reason why in long-term experiments on calcareous soils PAPR is always lower than MCP, soluble P fertilizer, in total yield of crops and P uptake by crops.

In this experiment, it is also clear that all PAPR treatments except Treatment S30 were close to MCP in yield for the first harvest and then getting significantly lower than MCP, which obviously differs from what was on acid soil. On acid soil, the longer an experiment lasted, the higher the effectiveness of PAPR rose till it came close to that of MCP.

It is also learnt from this experiment that on calcareous soils PAPR high in acidulation degree can meet with crop response similar to that soluble P fertilizer can within a short period of time. With the time going by, however, its crop response will drop down significantly. Therefore, from a long point of view, it is not a best choice to apply PAPR on calcareous soils.

Chapter 13. Interactions of the Two Major Components of PAPR in Soils

PAPR is made up mainly of monocalcium phosphate and unreacted phosphate rocks. It is, therefore, important to get to know how monocalcium phosphate reacts in soil in order to understand reaction of PAPR in soil.

13.1 Reaction of monocalcium phosphate in soil

The phase diagram of aqueous monocalcium phosphate solution (Brown, et al., 1959) showed that monocalcium phosphate was undergoing incongruent dissolution in water, that is to say, the ion composition of the solution differed from that of the solid. Once monocalcium phosphate is applied into the soil, fertilizer granules absorb moisture from the soil and even in relative dry soils and thus monocalcium phosphate dissolves, forming saturated solution (Table 13-1).

Table 13-1 Composition of the saturated hydrolytic solutions (Sample, et al., 1980)

Phosphate	Formula	Composition		
		pH	P(mol/L)	Ca(mol/L)
Monocalcium phosphate	$Ca(H_2PO_4)_2 \cdot H_2O$	1.0	4.5	1.3
Dicalcium phosphate	$CaHPO_4 \cdot 2H_2O$	6.5	0.002	0.001

In such a solution, phosphate radical ions are much higher than they ought to be whereas calcium ions are much less than they ought to be in the solution. In solid residual, however, more phosphate ions are released while calcium ions are relatively enriched. When monocalcium phosphate granules absorb adequate moisture, the saturated solution diffused outward and the remaining monocalcium phosphate gradually turns into dicalcium phosphate ($CaHPO_4$). The existence of phosphoric acid in the hydrolytic solution lowers pH of the equilibrium solution to 1 or so. The reaction can be expressed with the following equation:

$Ca(H_2PO_4)_2 \cdot H_2O + XH_2O \rightarrow CaHPO_4 + H_3PO_4 + (x + 1)H_2O$

As the concentration of phosphate ions in the form of H_3PO_4 in the solution within the fertilizer granules is much higher than that in the surrounding soil, thus forming a high concentration gradient, which facilitates diffusion of phosphate ions to the soil surrounding the granules. The dicalcium phosphate remaining in the fertilizer granules may continue its incongruent dissolution and then form apatite. The reaction can be expressed as follows:

$10CaHPO_4 + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4H_3PO_4$

Nevertheless, the above said reaction goes on very slowly with a very limited amount of H_3PO_4 formed, because $CaHPO_4$ is much lower than monocalcium phosphate in solubility in water. Its solubility constant K is 2.18×10^{-7} whereas the constant of monocalcium phosphate is 7.19×10^{-2} and that of hydroxyapatite $10^{-11.5}$. As a result, in the equilibrium solution the concentration of H_2PO_4 is very low and so is the gradient and diffusion of phosphate ions to the surrounding soil.

While the saturated solution of monocalcium phosphate is diffusing towards the surrounding soil, it dissolves a certain amount of Fe, Al, Ca, Mg, Mn, and some other cations. As the phosphate concentration of the saturated solution is far too higher than the solubility product constants of these cations commonly observed in the soil, they begin to precipitate on the path of diffusion of the saturated solution. In acid soils they precipitate mainly in the form of Fe – P and Al – P while in calcareous soils high in pH in the form of dicalcium phosphate and dimagnesium phosphate, which will then gradually turn into $Ca_8H_2(PO_4)_6$ (Sample, et al., 1980). It is clear that monocalcium phosphate undergoes the above-said series of reaction in the soil, forming a series of reaction products different in properties. The effectiveness of monocalcium phosphate in the soil will, therefore, be determined by these products.

13.2 Reaction of PAPR in soil

As PAPR is composed mainly of monocalcium phosphate and unreacted phosphate rocks, its soluble portion (monocalcium phosphate) reacts in the soil just like superphosphate (Garbouchev, 1981; Marwaha, 1983). What is different between them is that in PAPR the saturated solution and $CaHPO_4$ produced out of monocalcium phosphate may enter into further reaction with unreacted phosphate rocks in the fertilizer granules, thus generating more available P whereas with water soluble P fertilizers like superphosphate or tri-superphosphate, the saturated solution reacts first with Fe, Al, Ca, etc. in the soil and form insoluble compounds while diffusing (Hagin, 1985: Rajan, 1985; Hammond, et al., 1986). This reaction has had indirect experimental proof (Logan, et al., 1977; Mokwunye et al., 1980). As early as in 1957, Nordengren (cited from

Stephen, 1986) assumed that when PAPR was applied into the soil, its monocalcium phosphate hydrolyzed forming H_3PO_4, which might react further with unreacted phosphate rocks, producing additional monocalcium phosphate. He held that this assumption might explain why on acid soils Kotka fertilizer (PAPR) was equal to superphosphate in effectiveness. Although this assumption has been accepted by some scholars, different opinions do exist in the academic circle. Rajan (1985) conducted some experiments, revealing reaction between hydrolysate of monocalcium phosphate and unreacted phosphate rocks. But the experiments carried out by Mcsweency (1985) and Golden, et al. (1991) showed that there seemed no significant reaction between them. Terman, et al. (1967) got similar results from their experiments. Golder (1991) studied reaction between H_3PO_4 and PAPR out of phosphate rocks from North Carolina in the soil. He discovered that acidic hydrolytic solution of monocalcium phosphate in PAPR (20% and 50% in acidulation degree) moved towards surrounding soil in a pattern similar to that it did in 100% acidulated TSP. It made the soil in the vicinity of the fertilizer granule lower in pH, and dissolved soil minerals. Through the electronic microscope dissolution of primary minerals could be observed (Golden, et al., 1991). In two days the solution moved 6 ~ 14mm outword, depending on soil. The amount of P moving along with the solution made no substantial difference between fertilizers 50% and 100% in acidulation degree, but varied sharply from soil to soil.

Within the range the solution reached, phosphate soluble in 0.5M NaOH solution increased, indicating formation of Fe – P and Al – P, and complex compounds containing P, Ca, Al, Fe and Si were identified instead of simple ferric aluminum phosphate. Soil pH was then determined by two factors: acidic saturated solution introduced in with fertilizer and increased OH as a result of soil adsorption of P. Where the amount of ferric aluminum phosphate formed was the highest, pH decreased the least. The amount was directly related to acidulation degree of PAPR.

Researches by mineralogical methods (Golden, et al., 1991) revealed that when PAPR was applied into the soil, its monocalcium phosphate dissolved quickly and moved outwardly. Deposit of $CaHPO_4 \cdot 2H_2O$ was found on residual phosphate rocks, interface between the fertilizer and the soil as well as soil pores. Morphology of the deposit could clearly be seen through the electronic microscope. The amount of the deposit varied with the acidulation degree within a certain range of acidulation degree. No solid evidence, however, was found showing secondary dissolution of residual phosphate rocks with the saturated solution of monocalcium phosphate. Besides, the research also revealed that the mean particle size of residual phosphate rocks in PAPR increased, which indicates that smaller particle of rocks had priority in acidulation process and disappeared first.

13.3 Biological experiments

It is generally held that the two major components of PAPR and the interaction between them contribute positively in two aspects. 1) In chemical reaction. When monocalcium phosphate in PAPR undergoes incongruent dissolution, forming strongly acidic saturated solution with pH down to 1.0. Such solution may dissolve unreacted phosphate rock powder of PAPR, thus increasing the content of available P in PAPR (Mclean, et al., 1964); and 2) in biological action. The portion of soluble P in PAPR may supply the plant with P at its early growing stage, promote development of its root system and enable it to absorb more P from the unreacted phosphate rock in the PAPR. This is the so-called biological stimulating effect (Swart, et al., 1987; Chien et al., 1988).

For instance, Rajan, et al. (1992) prepared a PAPR from North Carolina phosphate rocks, with acidulation degree of 30%, 40% and 50%, separately using H_3PO_4 and had them applied into an acid soil (pH5.8) high in P fixation capacity. He found that PAPR, though different in acidulation degree, showed higher crop response from forage grass in yield than into water soluble P fertilizers and phosphate rocks did. He believed that the portion of water soluble P in PAPR stimulated growth of root systems, which then played an enhanced role in utilizing residual phosphate rocks in PAPR. The author holds that if the reactivity of the residual rocks in PAPR is dulled in acidulation, the positive effect of stimulating growth of root systems will compensate the above negative effect.

Different opinions about chemical reaction have been discussed in the previous paragraph. In order to make further clear what were chemical reactions and biological response, biological experiments were carried out to achieve more knowledge about the beneficial reactions between the two major components of PAPR and the biological behavior in the plant.

13.3.1. Material and method

a Soil:

The experiment used two typical types of red soils derived from the Quaternary red clay (Soil 1) and the Tertiary red sandstone (Soil 2), separately. The former was heavy in texture and high in P fixation capacity whereas the latter light and low. Both of the two soils were collected from Yingtan of Jiangxi. Their basic properties are now listed in Table 13 – 2.

Table 13-2 Basic properties of the soil used

Proerties	Soil 1	Soil 2
pH (H_2O)	4.8	5.0
Organic matter (g/kg)	5.6	4.1
Clay (< 2 μm %)	43.9	16.8
Total N (g/kg)	0.39	0.26
Total P (mg/kg)	214	69
Bray – 1 P (mg/kg)	1.6	2.5
Fe_2O_3 (mg/kg)⁽¹⁾	574.6	139.0
Al_2O_3 (%)⁽²⁾	2.55	1.06
CEC (cmol/kg)⁽³⁾	13.21	6.51
	Exchangeable cation (cmol/kg)	
Ca	2.75	2.34
Mg	0.52	0.32
K	0.24	0.12
Na	0.70	0.80
Base saturation (%)	32	55

Note: (1) extracted in $Na_2S_2O_4$ solution (pH7.3); (2) extracted with 0.5 mol/L NaOH solution; and (3)determined with neutral 1 mol/L NH_4Ac method.

b Phosphate rocks:

The phosphate rocks used for the experiment came from Jingxiang of Hubei. It is generally held that they are low in reactivity and grade, but high in MgO content and reserve. They are not suitable for direct acidulation but good for production of calcium-magnesium phosphate. Listed in Table 13 – 3 are chemical properties of the phosphate rocks from

Jingxiang of Hubei.

Table 13-3 Chemical properties of phosphate rocks from Jingxiang of Hubei

Item	%
Total P (P_2O_5)	19.36
CaO	33.0
MgO	5.55
SiO_2	23.2
Fe_2O_3	1.98
Al_2O_3	2.15
Na_2O	0.39
K_2O	0.62

c Pot experiment:

The experiment was designed to have 6 treatments: 1) CK (no P), 2) Phosphate rock powder containing 100 mg·P was mixed evenly with all the soil (1 kg) in the pot, 3) Superphosphate containing 100 mg·P was mixed evenly with all the soil (1 kg) in the pot, 4) Superphosphate containing 100 mg·P was mixed evenly with half (0.5kg) of the soil and the other half had no P applied. The two halves were put into a pot and separated from each other with a piece of filter paper vertically in the middle. When the pot was set, the piece was carefully pulled out. 5) Superphosphate (100 mg·P), phosphate rock powder (100 mg·P) and soil (1kg) were mixed evenly. 6) Superphosphate (100 mg·P) was mixed evenly with half (0.5kg) of the soil and the other half with phosphate rock powder (100 mg·P). The two mixtures were then put into the pot in the same way as in Treatment 4.

Besides, each treatment received 100 mg/kg N (urea), 50 mg/kg K_2O, 5 mg/kg Mg ($MgSO_4$) and microelements B and Zn.

The crop for test was ryegrass. The above-ground part was harvested twice, one month and two months after seedlings came out. The harvested parts were ashed at 525°C, which was then determined for P with the molybdate blue method.

13.3.2. Results

a Yields of the treatments

Difference between treatments in plant growth was already apparent when the seedlings just came out. Treatments 3, 4, 5 and 6 were far better than Treatment 1 (CK) and Treatment 2 in crop growth. Basically no beneficial effect was observed in Treatment 2, which indicates that this low reactivity type of phosphate rock is not fit for direct application on gramineous plants.

In Treatment 4, ryegrass grew slightly bette in the half of the soil mixed with SSP than in the other half without P. But the three weeks after the germination of seedlings, the difference faded out.

In Treatment 5, ryegrass grew far better than all the other treatments (Table 13 – 4).

Table 13-4 Crop responses in treatments (g/pot)

Treatment	1st harvest	2nd harvest	Total
	Red soil derived from the Quaternary red clay		
1	0.07c*	0.15d	0.22c
2	0.16c	0.40d	0.56c
3	1.25b	1.12bc	2.37b
4	1.26b	1.04c	2.30b
5	3.26a	1.90a	5.16a
6	1.19b	1.47b	2.78b
	Red soil derived from the Tertiary red sandstone		
1	0.05d	0.11e	0.15d
2	0.07d	0.16e	0.24d
3	1.15c	1.43c	2.64c
4	1.04c	1.15d	2.19c
5	3.02a	2.36a	5.38a
6	2.27b	1.77b	4.04b

Note. If letters following figures are the same, their difference is not significant on 0.05 level.

On the red soil derived from the Quaternary red clay high in P fixation capacity, Treatment 6 did not show any better crop response than Treatment 4, which indicates that there is no stimulating effect, i.e. phosphate rock powder did not play much role in supplying P, while on the red soil derived from the Tertiary red sandstone low in P fixation capacity, such as effect may occur, and phosphate rock powder played a significant role in stimulating plant growth (Table 13 – 4).

It is interesting to note that on the red soil derived from the Quaternary red clay, Treatment 5 and Treatment 6 were just the same in rate and type of the fertilizers applied, and only different in pattern of the application, but varied sharply in crop response. As is shown in Table 13 – 4, the total yield was 2.78g/pot in Treatment 6, but 5.16g/pot, about 86% higher, in Treatment 5, which probably indicates that mixing superphosphate with phosphate rock powder generated some beneficial effect. Nevertheless, no substantial difference was observed between the two treatments on the red soil derived from the Tertiary red sandstone.

b P uptakes in treatments

In Table 13 – 5 listed are P uptaken by plants in different treatments.

It is clearly shown in Table 13 – 5 that significant differences existed between treatments in P uptake.

Treatment 2 was a bit higher than Treatment 1 (CK) in P uptake, but the difference is far from significance. Treatments 3, 4, 5 and 6 were all significantly higher than Treatment 1 or 2 in plant P uptake.

Table 13-5 P uptaken by ryegrass in different treatments (mg/pot)

Soil	Treatment	1st harvest	2nd harvest	Total
Red soil derived from the Quaternary red clay				
	1	0.04e*	0.11d	0.16d
	2	0.17d	0.57d	0.74d
	3	4.28c	2.55bc	6.36c
	4	5.39b	2.27c	7.66bc
	5	9.45a	3.61a	13.07a
	6	4.88bc	2.91b	7.79b
Red soil derived from the Tertiary red sandstone				
	1	0.03c	0.09d	0.13c
	2	0.06c	0.15d	0.21c
	3	4.05b	2.46c	6.70b
	4	4.33b	2.46c	6.79b
	5	9.53a	4.51a	14.04a
	6	9.08a	3.73b	12.81a

Note. If letters following figures are the same, their difference is not significant on 0.05 level.

Between treatments the same in P application rate but different in application pattern, difference in P uptake was significant. For instance, on the red soil derived from the Quaternary red clay, Treatment 4 is significantly higher than Treatment 3 in P uptake with the first harvest. When it came with the second harvest, the difference was not so obvious.

On the red soil derived from the Tertiary red sandstone low in P fixation capacity, no big difference existed between Treatment 3 and Treatment 4 in P uptake with both harvests. No big increase in plant P uptake was observed in Treatment 4 on both of the soils (Table 13 – 5) and no difference was there between Treatment 4 and Treatment 3 in yield of the plant on both of the soils, too (Table 13 – 4). On the red soil derived from the Quaternary red clay, the plant P uptake in Treatment 5 was almost twice as much as that in Treatment 6, whereas on the red soil derived from the Tertiary red sandstone, such a phenomenon appeared only with the second harvest (Table 13 – 4).

c Contribution of P of different sources

Although it is difficult to determine how much P each P source (soil, superphosphate and phosphate rock powder) contributed to the total amount of P the plant absorbed, it is feasible to roughly estimate P contributions by superphosphate and phosphate rock powder in the total plant P uptake, because the soils used in the experiment are very low in P content (total P and available P) and P contribution by the soil in each treatment might as well be taken as a constant. In Table 13 – 6 listed are apparent values of the proportions of P coming from different sources.

Table 13-6 Estimation of P supply to the plant from superphosphate and phosphate rock in different treatments

Soil	Treatment	P supply source (mg/pot)			
		Soil	SSP	PR	Total P supply
Red soil derived from the Quaternary red clay					
	1	0.16	-	-	0.16d
	2	0.16	-	0.58	0.74d
	3	0.16	6.20	-	6.36c
	4	0.16	7.50	-	7.66bc
	5	0.16	6.36	6.49	13.07a
	6	0.16	7.63	0	7.79b
Red soil derived from the Tertiary red sandstone					
	1	0.13	-	-	0.13c
	2	0.13	-	0.08	0.21c
	3	0.13	6.57	-	6.70b
	4	0.13	6.66	-	6.79b
	5	0.13	6.57	7.21	14.04a
	6	0.13	5.89	6.79	12.81a

Table 13 – 6 shows that the soil is extremely low in P content and too low to supply any P to crops. In Treatment 2, though P supply was limited but higher than in CK'in absolute amount, in statistics the two treatments were more or less the same in P supply. Consequently, the phosphate rock used did not show its effectiveness in such acid soils with high P fixation capacity. Water soluble P fertilizer (superphosphate), however, shows significant crop response no matter in what treatment. Its absolute P supply was nearly 10 times as much as the PAPR's. But Treatment 4 did not show any superiority to Treatment 3.

It is interesting to note that the P supply in Treatment 5 was almost twice as much as in Treatment 6 whereas the difference between them lay only in application pattern. In Treatment 5 SSP and PR were blended together with the soil while in Treatment 6 they were applied separately. This is another indicator that on such acid soils with high P fixation capacity, the application method in Treatment 5 significantly increased P supply. But Treatment 6 and Treatment 4 were more or less the same in P supply, which indicates that the P supply of phosphate rock did not increase when SP and PR applied to half of the soil separately.

Let us take another look at the red soil derived from the Tertiary red sandstone low in P fixation capacity.

What is common to the red soil derived from the Quaternary red clay is that the soil per se is low in P supply and direct application of phosphate rock did not help much increase P supply.

It is noteworthy that P supply in Treatment 6 was almost twice as much as in Treatment 4, which indicates that on the condition that phosphate rock and superphosphate were applied separately in half of the soil to exclude any possible interaction between them, P supply of PAPR increased almost twice. Meanwhile, P supply did not increase when the two fertilizers were applied in mixture, which indicates that even if the two fertilizers are mixed there seems to be no significant beneficial interaction between them.

13.4 Discussion

From the data in Table 13 – 4 (crop yield), Table 13 – 5 (P uptake) and Table 13 – 6 (P sources), it can be inferred that direct application of phosphate rock (Treatment 2) on the two soils used did not show any meaningful crop response and there was no significant statistical difference between Treatment 2 and Treatment 1 (CK) in yield and P uptake.

Water soluble P fertilizer (superphosphate), no matter in what treatment, met with significant crop response. But there was no significant difference between treatments different in application pattern.

On the red soil derived from the Quaternary red clay, Treatment 4 and Treatment 6 were more or less the same in yield and P uptake, which indicates that addition of phosphate rock to Treatment 4 would not show any beneficial effect. But it is interesting that when phosphate rock was applied in mixture with superphosphate, crop response and P uptake increased significantly, which can only be interpreted as mixture with superphosphate increasing effectiveness of PAPR. The cause of the increase may coincide with the presumption of the predecessors that on acidic red soils with high P fixation capacity, the hydrolysis solution of monocalcium phosphate might react first with phosphate rock powder, thus increasing effectiveness of the PAPR and avoiding reaction between the saturated solution and the soil generating a large amount of active Fe and Al, which might fix a large amount of existing soluble P, thus lowering effectiveness of the fertilizers. This positive effect did not really appear on the red soil derived from Tertiary red sandstone low in P fixation capacity. For instance, there was no difference between Treatment 5 and Treatment 6 in P uptake and the difference in yield was too small to be noticeable statistically, which may indicate that on soils low in P fixation capacity, the above-said useful reaction between monocalcium phosphate and phosphate rock may exist, but not too much.

What is noteworthy is that on the red soil derived from the Tertiary red sandstone, Treatment 6 was much higher than Treatment 4 in P uptake. As in Treatment 6 the two P fertilizers were applied separately to half of the soil, interaction between them was excluded. In this case, the effectiveness of PR was greatly increased, which may serve as evidence that “biologically stimulating effect” exists (Swart, et al., 1987). That is to say, soluble P stimulates early development of the root system, which later becomes more effective to use of the source of hardly soluble P, thus raising the effectiveness of PAPR. The comparison between Treatment 3 and Treatment 5 also shows existence of similar effect. The effect, however, did not display itself on the red soil derived from the Quaternary red clay with high P fixation capacity, i.e. Treatment 4 and Treatment 6 were more or less the same in P uptake.

To sum up, it may be held that interaction exists between the two major components (monocalcium phosphate and phosphate rock powder) of PAPR and this type of interaction can be presumably sorted into two, chemical and biological. The chemical one is a result of hydrolysis of monocalcium phosphate (incongruent dissolution), which generates strongly acidic saturated solution, which helps reduce the fixation of soluble P in soils with high P fixation capacity, thus raising the effectiveness of PAPR as a whole. The biological reaction is that the existing soluble P in P-deficient soils stimulates early development of root systems of the crop, which will increase the ability of the crops to use hardly soluble P, such as phosphate rock powder.

The chemical action will be effective mainly on acid soils high in P fixation capacity whereas the biological action on P-deficient soils low in P fixation capacity.

Chapter 14. Main factors influencing effectiveness of PAPR

Factors influencing effectiveness of PAPR are multiple. The most interesting issue in discussion is whether or not useful reaction exists between the two major components of PAPR. The issue has actually been elaborated in the preceding chapter and will not be discussed here again. Obviously, it exists in some soils, but in some soils, even if it does exist, there is also a question pops up whether the reaction is strong enough to show apparent crop response (yield increase). Some authors (McSwechey, et al., 1985) hold that the saturated hydrolytic solution of monocalcium phosphate can only dissolve 4 ~ 6% of the residual phosphate rock of PAPR, thus producing only a limited amount of soluble P. Of course, dissolution is associated with a series of factors, such as acidulation degree, reactivity and grade of phosphate rocks, etc.. It is inadvisable to treat different matters as the same. The following space will be devoted to discussion of other factors than the above-described reaction.

14.1 Type of acids used and degree of acidulation

Acids used to produce PAPR are mainly H_2SO_4 and H_3PO_4 or their mixture. What type of acid to be used will have certain effect on properties and effectiveness of the fertilizer.

14.1.1. Effect on properties of the product

PAPRs using different acids, even if acidulated to the same degree, will be different in P form and content, for instance, total P and water soluble P content (Table 14 – 1, Chien et al., 1988).

Table 14-1 Effect of acidulation degree on P content of product

Rock phosphate	Acid used	Acidulation degree (%)	% (P_2O_5)		
			Total P	Water soluble P	CAP
	-	-	19.5	0	3.3
Pesca, Columbia	H_2SO_4	20	17.5	4.3	2.2
	H_3PO_4	20	25.1	8.8	3.9
	-	-	25.1	0	2.2
Mussoorie, India	H_2SO_4	50	18.2	9.0	1.0
	H_3PO_4	50	25.0	20.0	1.5

It is clearly shown in Table 14 – 1 that PAPR acidulated with H_3PO_4 is higher than that with H_2SO_4 in total P, soluble P and citric acid soluble P (CAP), though they have the same acidulation degree. This will certainly affect effectiveness of the product calculated on the basis of acidulation degree. In addition, when H_2SO_4 is used, total P in the product will decline with rise in acidulation degree. For example, when phosphate rocks 25.3% in total P (P_2O_5) are acidulated with H_2SO_4 to 30%, their product will be 24.5% in total P and when to 50%, it will be 18.0%.

In producing PAPR, impurities in the acid used will greatly affect effectiveness of the product. Bollan (1990) believed that amount and quality of the acid used would influence soluble P content in the product. For instance, impurities in H_3PO_4, such as Fe, Al, Mg, etc., may reduce the speed and actual degree of acidulation and those in H_2SO_4 will have similar adverse effect.

14.1.2. Impact on effectiveness

When phosphate rocks use the same type of acid for acidulation, acidulation degree will affect effectiveness of the product because its soluble P content varies.

Results of an eight-month pot experiment (Rajan, 1996) indicated that P uptake of ryegrass was significantly related to soluble P content of the PAPR produced.

Effectiveness of PAPRs different in acidulation degree is also correlated with duration of an experiment. In long-term experiments, the 20%, 35% and 50% acidulation degree PAPRs from North Carolina phosphate rocks were similar to TSP in effectiveness (cited from Hagin, et al., 1993) whereas in short-term experiments, PAPR of 20% acidulation degree was lower than TSP in effectiveness.

Some researchers discovered that PAPRs using different types of acid to the same acidulation degree were also different in effectiveness. Rajan, et al. (1994) found that PAPR using H_2SO_4 was lower than superphosphate in effectiveness, though its water soluble P accounted for 56% of its total P while H_3PO_4-acidulated PAPR with water soluble P accounting for 40% or 32% of its total P was the same as superphosphate in effectiveness on the same type of soil. They thought that when acidulated with H_2SO_4 PAPR had its granules coated with a thin layer of $CaSO_4$, thus affecting release of P. Hammond (1980) also observed a similar phenomenon that when acidulated to the same degree (20%), PAPR using H_2SO_4 contained far too much lower soluble P than that using H_3PO_4 and the generated $CaSO_4$ acidulated with H_2SO_4, cemented granules into hard lumps. Recent researches in India (Biswas, et al., 1998) also demonstrated that on neutral soils PAPR using H_2SO_4 (to 25% and 50%) was lower than that using H_3PO_4 (corresponding in acidulation degree) in effectiveness (yield and P uptake), but they were almost the same in residual effect.

Gani, et al. (1992, cited from Rajan, 1994) also found that in PAPR using H_3PO_4 unreacted phosphate rocks dissolved at a speed that increased with the decline of soil pH, whereas in PAPR using H_2SO_4 there was no such a phenomenon. He believed that it was attributed to the formation of a $CaSO_4$ coating.

Al-Fariss, et al. (1991) carefully studied the dissolving reaction of phosphate rocks by H_2SO_4 and H_3PO_4. They discovered that when the traditional dihydrate process used H_2SO_4 to acidulate phosphate rock, the surface of phosphate rock particles was covered with $CaSO_4$, but when H_3PO_4 was used, it was not.

The formation of $CaSO_4$ in using H_2SO_4 will not only affect effectiveness of the product, but also efficiency of the acidulation. For instance, in production when PAPR is dried at the temperature of 110°C, water soluble P content and effectiveness of the product will be lowered and at the temperature of 25 ~ 60 °C, nothing will be affected. Hence it is inferred that the main cause of effectiveness of the product being lowered is the formation of $CaSO_4$ that affects further dissolution of residual phosphate rock in product.

Someone recommended that a certain amount of KCl be added in the process of the production of PAPR to prevent formation of $CaSO_4$ with reaction as follows (Chien, 1989, lecture in China):

$$2KCl + H_2SO_4 \rightarrow K_2SO_4 + 2HCl$$

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$$

$$14HCl + Ca_{10}(PO_4)_6F_2 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2 \cdot H_2O + 7CaCl_2 + 2HF$$

The advantage of this method is the formation of $CaCl_2$ instead of $CaSO_4$ coating and introduce K, thus the product as a PK compound fertilizer, and its disadvantages are that it involves Cl^-, which is strongly corrosive to equipment and that moisture adsorption of $CaCl_2$ in the product makes the product wet and blocky and poor in physical properties.

14.2 Characteristics of phosphate rock used

The effect, being discussed here, of properties of phosphate rocks on effectiveness of PAPR has two connotations: one is effect of properties of the phosphate rocks used to produce PAPR and the other is effect of properties of the residual phosphate rock powder in PAPR.

14.2.1. Effect of properties of raw material phosphate rocks

Researches (Sale, et al., 1991) revealed that reactivity of phosphate rocks and their Fe and Al impurities contents heavily affect effectiveness of PAPR in relation to water soluble P fertilizers.

a Reactivity of phosphate rocks

PAPR prepared from phosphate rocks high in reactivity, like those from North Carolina, acidulated with H_3PO_4 to 30% was equal to superphosphate in effectiveness on perennial pasture grass (Machay, et al., 1990).

To make PAPR equal to superphosphate in effectiveness, phosphate rocks low in reactivity, like those from Florida, must be acidulated with H_3PO_4 to at least 50% (70% or more water soluble P). if they were acidulated with H_2SO_4 with water soluble P even up to 60%, crop response to their product was still lower than that to water soluble P fertilizers (cited from Rajan, et al, 1993).

Both field and pot experiments demonstrated that to make PAPR from phosphate rocks with high reactivity steadily equal to soluble P fertilizers in effectiveness, it must be made to contain soluble P at least 50% of its total P (Rajan, et al, 1993; Bations, et al., 1990).

PAPRs prepared from inactive phosphate rocks vary in effectiveness. Experiments conducted in IFDC, Australia and New Zealand revealed that generally these PAPRs were lower than soluble P fertilizers in effectiveness. But in India local phosphate rocks low in reactivity were used to produce PAPR (acidulated with H_3PO_4 to 20%), which is as good as superphosphate in effectiveness (Marwaha, et al, 1983, cited from Rajan, et al., 1993).

b Effect of impurities Fe and Al in phosphate rocks

Fe and Al contents in phosphate rocks may affect effectiveness of PAPR. When the contents are higher, the effectiveness of PAPR lower (Hammord, et al., 1989), which is because Fe and Al reduced solubility and availability of phosphate compounds. It is, therefore, essential to take this factor into account when choice is to be made of phosphate rocks as raw material for production of PAPR.

Fe and Al contents in phosphate rocks affect quality of PAPR. Researches indicate that of 14 PAPR products from7 different kinds of phosphate rocks acidulated with H_2SO_4 to 30% and 50% separately, content of soluble P is positively related to acidulation degree but negatively to content of Fe and Al in the rocks, which demonstrates that Fe and Al in the rocks may turn some water soluble P into hardly soluble phosphate in PAPR, in which content of citric acid soluble P will also decrease.

Researches also show that Fe and Al contents (0.7 ~

12.4%) in phosphate rocks directly affect effectiveness of PAPR. The latter goes down when the former go up (Hammord, et al., 1989). The major cause of the decline in effectiveness is that Fe and Al in phosphate rocks are dissolved during acidulation of the rocks and hence enabled to react with some newly formed soluble P, thus fixing some water available P. When PAPR is prepared by blending soluble P fertilizer with phosphate rock powder and making them into granules, this adverse effect may be greatly reduced, which has been demonstrated in experiments (Menon, et al., 1990). The author compared a blending product of phosphate rocks high in Fe and Al content (8.8%) and triple superphosphate with a PAPR from the same rocks using the acidulation method the results showed that the former is higher than the latter in effectiveness. When compared the products using phosphate rocks moderate in reactivity and low in Fe and Al content, they were very close in effectiveness.

Generally speaking, the requirement of Fe, Al impurities in phosphate rocks for production of PAPR is not as strict as for full acidulated P fertilizer. For instance, phosphate rocks from Kodjaxi, Africa containing 3.1% Fe_2O_3 and 4.0% Al_2O_3 is not fit for production of superphosphate because of wasteful consumption of H_2SO_4. But Chien (1989, lecture) thought that they could be used to produce PAPR of acidulation degree 50%.

14.2.2. Properties of residual phosphate rock in PAPR

Being one of the two major components of PAPR, residual phosphate rock is important for effectiveness of the product. Here involved are the following issues:

1) availability or reactivity of residual phosphate rock; 2) effect of properties of raw material rocks on effectiveness of PAPR, including phosphate rocks types and impurities; 3) residual effect of residual phosphate rock; and 4) dissolving effect of hydrolytic solution of water soluble P on residual phosphate rock. The last issue has already been addressed in the preceding paragraphs and will not be discussed here any more.

a Availability of unreacted phosphate rocks

In view of the important role of the unreacted phosphate rocks in PAPR in P supply, quite a number of researchers studied properties of this portion of PAPR(Braith Waite, et al., 1990; Charleston, et al., 1989; Junge, et al., 1989; Ressler, et al., 1989). In their studies, more of them used extraction methods, so what they may not be fully reflect the real situation of water soluble P, dicalcium and unreacted phosphate rocks in the rhizosphere of plants. Nevertheless, they got some useful knowledge.

Researches show that after PAPR being extracted with water, 2% citric acid solution, neutral or acidic ammonium citrate solution, its unreacted phosphate rocks are lowered in reactivity (citric acid or formic acid soluble available P) to a certain extent that is positively related to its acidulation degree. Although Charleston, et al. (1989) found that at lower acidulation degree, for example, at 20% with H_3PO_4 reactivity of unreacted phosphate rocks lowered the most. The drop might be attributed mainly to formation of iron phosphate, aluminum phosphate, $CaSO_4$ and CaF_2 coatings and, to some extent, to change in crystal structure of phosphate rocks. Besides, as acidulation first with the portion of phosphate rocks high in reactivity, the left is probably low in reactivity. But some people hold different views. Resseler, et al. (1989) stated that availability of unreacted phosphate rocks was obviously much lower than that of the original rocks. Others held that specific surface of unreacted phosphate rocks would increase during acidulation, thus expanding the area for reaction and hence raising the reactivity of the residual rocks, because he believed that acidulation would leave pits on the surface of the unreacted rocks. This assumption, however, has not proved with experiment. Observations before and after acidulation through scanning electronic microscope did not find much change in the surface of phosphate rocks (Stesher, et al., 1986).

Acidulation with H_2SO_4 produces some $CaSO_4$, which may form coating over the unreacted grains of phosphate rocks, thus retarding its dissolution of and lowering availability of it. Researches also revealed that P release from unreacted phosphate rocks in PAPR is positively related to reactivity of the original rocks (Hagin, et al., 1990), i.e. properties of the original phosphate rocks influence reactivity of the residual rocks.

Electron-beam microanalysis revealed that in PAPR unreacted rocks were covered with a layer of coating high in F (Resseler, et al., 1989). This may be of the major reasons why unreacted phosphate rocks are lower in reactivity and availability than the original rocks. However, there are some phosphate rocks, like those from North Carolina, whose reactivity remain the same after acidulation.

The importance of reactivity of residual phosphate rocks may be alleviated in the following two situations:

- The soil is very acidic (pH < 5). Even if the unreacted phosphate rocks in PAPR are very low in reactivity, they can efficiently supply P.
- The soil has strong affinity for Calcium.

In these two cases, even if phosphate rocks are very low in reactivity, they can show significant crop response.

b Effect of some soil properties on effectiveness of PAPR

Soil properties that may affect effectiveness of PAPR include soil pH, Ca saturation, Al saturation, P content, P fixation capacity, etc.. The first three items are closely related to soil acidity. Here in this chapter the space will be devoted to effect of soil Ca, pH and P fixation capacity.

Effect of soil pH and soil P level

It was reported that PAPR had good crop response not only on acid soils but also on neutral and calcareous soils (Garbouchev, 1981; Hagin, J. 1985). If it is true, it indicates that soil pH and soil Ca will not affect effectiveness of PAPR. This holds, however, only conditionally. For instance, it is possible for PAPR to have good crop response on neutral and even calcareous soils if its original phosphate rocks are very high in reactivity and the crop has strong ability of utilizing P. Nevertheless, field experiments (Rajan, et al., 1994) demonstrated that on acid soils, only pH ranging between 4.2 and 6.3 facilitated dissolution of unreacted phosphate rocks, and that PAPR had good crop response from forage grasses.

The effect of soil pH on effectiveness of PAPR functions in two aspects: on availability of soluble P, which has already been elaborated in a large number of papers and will not be dealt with any more in this book, and on availability of P in unreacted phosphate rocks of PAPR, in which soil P fixation capacity is also involved. Ghani, et al. (cited from Rajan, et al., 1993) found that on soils moderate in P fixation capacity, pH did not affect effectiveness of PAPR and on soils high in P fixation capacity higher pH would reduce effectiveness of PAPR using H_3PO_4 for acidulation, probably because higher pH affected solubility of phosphate rock (pH5.0 ~ 6.5). PAPR using H_2SO_4 for acidulation, however, was not affected. It may be thought that the $CaSO_4$ coating formed during acidulation and the transformation after PAPR is applied into the soil affect solubility of phosphate rocks and hence pH has nothing to do with reduced effectiveness. As soil pH affecting effectiveness of PAPR often involves soil P fixation capacity, the spaces below will be spared for some related issues.

Rajan, et al. (1986) studied effect of soil P level on effectiveness of PAPR, discovering that on soils low in P level, only PAPR with acidulation degree up to 50% could be compared with water soluble P fertilizers in effectiveness, while on soils high in P level PAPR with acidulation degree to 30% was almost as good.

Soil P fixation capacity

Among the soil factors affecting effectiveness of PAPR, soil P fixation capacity has been a subject that attracts more attention (referring to Sanyal, et al., 1991). They hold that on soils high in P fixation capacity and acidic in reaction always high in Fe and Al concentration in soil solution, after water soluble P fertilizer is applied, a large amount of water soluble P is fixed, and this fixation reaction will be more severe due to further dissolves soil Fe and Al by hydrolytic solution, thus leading to decline in effectiveness of the fertilizer. However, when powdered PAPR low in acidulation degree (acidulated with H_3PO_4 to 10 ~ 20%) is used, it can compare with and even exceed TSP in effectiveness. On 6 soils different in P fixation capacity, effectiveness of PAPR goes up with rise in P fixation capacity. PAPR is equal to superphosphate in effectiveness on soils with P fixation capacity being 28% ~ 36%, and exceeds superphosphate on soils higher in P fixation capacity. Others have discovered that on soils low in P fixation capacity, PAPR 100% in acidulation degree is the best choice and on soils moderate in P fixation capacity, PAPRs with acidulation degree ranging from 20% to 100% make no difference in effectiveness (Melean, et al,. 1970).

Chien, et al. (1989) found that relative effectiveness of PAPR, in the form of either dry matter yield or plant P uptake, increases with P fixation capacity. When the soil P fixation capacity ranged between 28% and 36%, PAPR and superphosphate were the same in crop response and when the soil P fixation capacity exceeded 36%, the former would have a better crop response than the latter.

Mclean, et al. (1964, 1965, 1879) published a series of papers, stating that on soils low in P fixation capacity fully acidulated fertilizers (superphosphate) were better than PAPR whereas on soils high in P fixation capacity, PAPR with certain acidulation degree might become equal to water soluble P fertilizers in effectiveness. The reason of their statement is that when water soluble P fertilizers are used, a large proportion of soluble P is fixed by a large amount of active Fe and Al in the soil. As a result, its effectiveness is greatly lowered. When PAPR is applied, the monocalcium phosphate in the fertilizer is hydrolyzed, forming H_3PO_4, which then comes first to react with unreacted phosphate rocks in the fertilizer, forming $CaHPO_4$, which is available to plant in acidic soils. At the same time, most of the H_3PO_4 generated through hydrolysis is neutralized through reacting with unreacted phosphate rocks, thus reducing the amount of acid that otherwise will dissolve Fe and Al in the soil and hence reduce the P fixation ability of the soil. That is why on soils high in P fixation capacity, PAPR can be as good as or even better than superphosphate in effectiveness.

There is another explanation of why on soils moderate – high in P fixation capacity, PAPR is similar to TSP in effectiveness. 1) on soils high in P fixation capacity, a large proportion of soluble P in TSP is fixed, thus lowering its effectiveness; 2) a smaller proportion of soluble P in PAPR is fixed; and 3) the soluble P in the fertilizer per se and $CaHPO_4$ formed during hydrolysis, makes the PAPR to keep a relative high P concentration in soil solution.

Mokwunye, et al. (1980) discovered that P from PAPR was fixed by soil with a less extent than P from water soluble fertilizers. for instance, on three types of tropical soils, PAPR acidulated with H_3PO_4 to 20% and TSP were applied at the same rate on the basis of water soluble P, the soil in the PAPR treatment had more water soluble P than the one in TSP treatment. The phenomenon became more significant with increase in soil P fixation capacity.

Misra, et al. (cited from Stephen, 1986) also found similar results. On soil (latosol pH 4 with high content of active Fe and Al) the total yield of three consecutive crops applied with PAPR (H_3PO_4 to 20%) was higher than that with PAPR (H_3PO_4 over 50%) or TSP, whereas on soil with pH being 5.6 the total yield with PAPR (H_3PO_4 10% or 20%) was lower than that with PAPR (H_3PO_4 over 50%) or TSP. On soil with pH at 6.5, the yield increased with the acidulation degree of PAPR.

It can, therefore, be inferred that on soils low in P fixation capacity water soluble P fertilizers may be higher than PAPR in effectiveness. Dissolution of unreacted phosphate rocks in PAPR may be retarded due to existence of a large amount of water soluble P formed from hydrolysis of monocalcium phosphate in the vicinity (common ion effect). It is not until these P is absorbed by plants or transformed into hardly soluble P that unreacted phosphate rocks will begin to dissolve. Hence on soils low in P fixation capacity whether PAPR is lower than or equal to TSP in effectiveness depends on dissolution of unreacted phosphate rocks and duration. In short-term experiments or experiments conditioned unfavorable for dissolution of unreacted phosphate rocks, PAPR may be lower than water soluble P fertilizers in effectiveness. This may explain the statements in some papers that TSP is higher than PAPR in effectiveness. Long-term experiments, however, have enough time to dissolve the unreacted phosphate rocks. In this case, PAPR will be as good as or better than water soluble P fertilizers in effectiveness.

Di (1991, cited from Rajan et al., 1993) used isotope in his experiment, which indicates that PAPR (H_3PO_4 to 30%) could keep soil exchangeable isotope P at a stable level while monocalcium phosphate could not. He held that this was the result of reduced P fixation by PAPR or continued dissolution of unreacted phosphate rocks.

Others believe that the effect of soil P fixation capacity may be associated with soil pH. Some researches show that with increase in soil P fixation capacity, soil pH decreases. It is, therefore, held that the effect of soil P fixation capacity on PAPR effectiveness is not only because PAPR reduces soil P fixation, but also reduction of soil pH thus increases the dissolution of residual phosphate rocks (Rajan, et al., 1993).

Chapter 15. Discussion and Conclusion

Although PAPR has already had a history of 70 years and quite a number of countries, including some developed West European countries, have produced and applied the fertilizer, PAPR is a relatively new type of fertilizers and it is still an issue worth discussing what is the future of PAPR in China. The discussion consists of three parts in the following paragraphs.

Basic evaluation of PAPR

Conditions for China to develop PAPR

Effectiveness of PAPR and its conditions

15.1 Basic conditions for China to develop PAPR

In comparison with fully acidulated P fertilizers, PAPR has some features, which may just serve as favorable conditions for China to develop this type of fertilizers.

Production of PAPR saves sulfuric acid and/or phosphoric acid. To produce PAPR 50% in acidulation degree (H_2SO_4), each ton of the product saves 40% or so of H_2SO_4 (refer to Chapter 6). According to prediction of some relevant agencies, by 2005 the yield of H_2SO_4 in China will be 26.875 million tons, which will be far from enough, leaving a gap of 0.89 million tons (《P Compound Fertilizers and Phosphoric acid Information》 2000, No. 1, pp. 7). It is, therefore, of great practical significance for China, a country not very rich in S resources, to develop sulfuric acid- and phosphoric-acid-saving PAPR.

To a certain extent, some phosphate rocks unfit for producing fully acidulated P fertilizers may be used to produce PAPR. For instance, some countries have succeeded in producing PAPR (H_2SO_4 to 50%) from phosphate rocks high in Fe, Al and other impurities (3.1% Fe_2O_3 and 4.0% Al_2O_3) which unfit for producing superphosphate and (Chien, S.H., 1989, lecture in China). Of course, it does not necessarily mean that all the phosphate rocks unfit for fully acidulated P fertilizers can used to produce PAPR. Phosphate rocks containing too much detrimental impurities are also unfit for producing PAPR.

From the viewpoint of economy, direct application of phosphate rock powder is the most economical. Yet not all phosphate rocks can be used for direct application in the form of powder as fertilizer. Some phosphate rocks show good crop response. For instance, phosphate rocks from Sechura of Peru are equal to 80% of TSP in effectiveness when applied direct in the form of powder (Chien, S. H., 1989). Phosphate rocks from Morocco and North Carolina of the USA are also very good. But in China most phosphate rocks are low in reactivity, their effectiveness is not as desirable (refer to Chapter 4). Under such a circumstance, to develop PAPR is a selectable option.

Development of blended compound fertilizers is an important orientation of China. In the process of producing blended compound fertilizers, it is unadvisable to have urea blended directly with superphosphate or TSP, because urea molecules will take place of crystallized water in the monocalcium phosphate in these P fertilizers, thus making the product wet and caking and hence hard to apply. In order to solve the problem, some producers adopt a pre-blending drying method, which will certainly increase cost of the product. Some ammonified superphosphate or TSP to 5% or so, which may lead to higher pH of the product, thus turning monocalcium phosphate into dicalcium phosphate and hence lowering the solubility of the product. PAPR, however, does not have such a problem when blended with urea. Because it contains less monocalcium phosphate, not enough crystallized water would be displaced to make a serious problem of wetting and caking. Of course, when PAPR contains too much free acid and water, it can not be blended with urea.

The general production process of PAPR is rather simple. The equipment for producing superphosphate can easily turn to production of PAPR. In China there are a huge number of small- and moderate-sized superphosphate factory. If PAPR factory are to be set up in the vicinity of those suitable phosphate deposits by making use of existing equipment for superphosphate, the cost would be much lower.

It has been fully demonstrated in this research that a part of the moderate- and low-graded phosphate rocks in China are suitable for PAPR production, this corresponds to 78% of China's phosphate rocks reserves. Consequently, the development of PAPR may be one of the approaches to making full use of the P resources of China.

China has a large area of acid soils on whch PAPR displays the better effectiveness and residual effect.

15.2 Effectiveness of PAPR

15.2.1. Effectiveness and residual effect

Based the results of the field experiments (65 scattered over 6 provinces and involving 10 crops) and pot experiments (6, half of which lasted for 6 cropping seasons), it can concluded as follows:

On acid soils, in most experiments the effectiveness of PAPR from phosphate rocks with moderate or low reactivity acidulated to 50% or so with H_2SO_4 equal to 93 ~ 96% that of superphosphate or TSP, when acidulated with mixed acid (H_2SO_4 + H_3PO_4) to 45% it will have 96 ~ 98% and when acidulated to 75%, almost the same as water soluble P fertilizer (in 10 field experiments).

On acid soils, residual effect of PAPR reaches 100% of fully acidulated P fertilizers.

On calcareous soils, it is hard for PAPR to be equal to fully acidulated P fertilizers in effectiveness.

On acidic paddy soils, PAPR from phosphate rocks high in reactivity (like Moroccan rocks) will have nice crop response even if its acidulation degree is low (15% with H_2SO_4 in the experiment). But on neutral and weakly acidic paddy soils, PAPR 30% in acidulation degree fails to compete with fully acidulated P fertilizers.

Generally speaking, on acidic paddy soils with upland crops, PAPR from phosphate rocks with moderate in reactivity acidulated to 50% will be close to fully acidulated P fertilizers in effectiveness.

On acid soils, PAPR from phosphate rocks low in reactivity, like from Jinping, even if acidulated with H_3PO_4, can hardly catch up with fully acidulated P fertilizers in effectiveness.

15.2.2. Issues related to effectiveness

It is generally held that on acid soils, the higher the soil P fixation capacity, the more favorable for PAPR to display its effectiveness. This assertion, however, is conditional. The experiments in China, on red soils high in P fixation capacity, PAPR, acidulated even up to 60% with H_2SO_4, is still behind fully acidulated P fertilizers in effectiveness. In such a case, granulation of PAPR may help PAPR overcome the adverse effect of P fixation and display higher effectiveness, which may be close or equal to that of fully acidulated P fertilizers.

It was discovered that when PAPR was close or equal to fully acidulated P fertilizers in yield of crops, the former was still lower than the latter in P uptake. Does this phenomenon show that the productivity (biomass formed per unit P absorbed by plant) of the P in PAPR is higher or that plant can not get as much P supply from PAPR as from fully acidulated P fertilizers? This is an issue which deserves further study.

The Effect of unreacted phosphate rock in PAPR.

Field experiments show that PAPR always displays high effectiveness in soils low in pH, no matter whether on upland soils or paddy soils, which indicates that soil acidity plays an important role in stimulating dissolution of unreacted phosphate rocks in PAPR. This is also the major cause why its residual effect (relative value) is often higher than its relative effectiveness on the first crop. The experiments also demonstrate that phosphate rocks, particularly high in reactivity, show significant dissolution reaction.

As for dissolution of unreacted phosphate rocks caused by hydrolysis of monocalcium phosphate in PAPR, we believe that this reaction does exist. Nevertheless, several phenomena in the experiments indicate that it is better not to overestimate this effect on effectiveness of PAPR. The phenomena are:

On calcareous soils, no significant dissolution of unreacted phosphate rocks was detected.

Soil acidity shows significant effect on effectiveness of PAPR. On neutral soils, PAPR is, in most cases, obviously behind fully acidulated P fertilizers in effectiveness.

Why can PAPR be close to or even exceed fully acidulated P fertilizers in effectiveness on certain conditions? Besides soil acidity, some authors believe that there are the following several probabilities (Yeates, et al., 1993; Logan, et al., 1977):

In PAPR, the saturated hydrolytic solution of monocalcium phosphate may dissolve some unreacted phosphate rocks, though different opinions do exist.

Acidulation has expanded surface area of the unreacted phosphate rocks in PAPR.

Higher soil P fixation capacity enables PAPR low in acidulation degree to display higher effectiveness. Then comes a conclusion that on soils different in P fixation capacity, different acidulation degree may be used. On soils low in P fixation capacity, PAPR of 100% acidulation degree is the best choice. On soils moderate in P fixation capacity, 20% in acidulation degree is just the same as PAPR 100% in acidulation degree. And on soils high in P fixation capacity, PAPR 20% in acidulation degree is good enough.

PAPR contains both readily and slowly available phosphate, which may have “start effect”.

Pot experiments with soil light in texture from Australia show that leaching loss of P was less from PAPR than from fully acidulated P fertilizers.

Researches indicate that diffusion distance of P from PAPR 20% in acidulation degree is longer than that from fully acidulated P fertilizers.

Of course, there are more other sayings.

It can be held that the above-listed factors may more or less exist under different conditions, but their effect varies with the condition.

15.3 Economic significance of PAPR

Based on the economic analysis of the production of PAPR in China in Chapter 6, it is held that cost of a PAPR, 50% in acidulation degree (H_2SO_4) and relative effectiveness over 90%, will cost about 75 ~ 78% as much as superphosphate does and save the consumption of H_2SO_4 by 40%.

According to the estimation by IFDC, PAPR 50% in acidulation degree (H_2SO_4) is about 80% of superphosphate in production cost and saves 50% of H_2SO_4. This estimation is quite close to what we have got in Chapter 6 (Chien, S.H., 1989, lectures in China).

15.4 Suggestion about the methods to determine available P in PAPR

The authors of the book has suggested a new concept of “Theoretically available P” of P fertilizer , which is defined as:

Theoretically available P =

$$\frac{\text{water soluble P applied}}{\text{Plant P uptake (from water soluble P fertilizer)}} \times \text{Plant P uptake by tested PAPR}$$

Based on this concept, comparison of different P fertilizers in terms of P availability and studies on changes in availability of a P fertilizer applied into different soils can be done. As the data are derived from the data of the plant per se, they can fully reflect the extent of P availability.

Here we are going to discuss what is the best method to determine available P of PAPR.

In Table 15 –1 (for sake of convenience, the data in the table are cited from Table 10 – 25) listed are a group of data from the pot experiments.

Table 15-1 Theoretically available P and P extracted with different extractant

Fertilizer	P uptake by plant (mg/pot)	P applied (mg/pot)			TAP* (mg/pot)
		Soluble P	2% CAP*	FAP*	
RPK	28.2	0.22	41.6	45.5	92.5
S30K	25.7	28.8	61.7	55.8	84.1
S60K	34.8	61.2	97.2	74.5	113.9
SP60K	38.5	105.8	124.2	114.3	126.0
C1	29.5	43.4	84.6	66.6	96.5

Note: * CAP stands for citric acid soluble P, FAP for formic acid soluble P and TAP for theoretically available P.

Based on the data in Table 15 – 1, correlation coefficients of the amount of P extracted with different extractant with the amount of theoretically available P can be worked out :

Between soluble P and theoretically available P, *r* = 0.89;

Between citric acid soluble P and theoretically available P, $r = 0.89$;

And between formic acid soluble P and theoretically available P, $r = 0.88$.

These indicate that significant correlationship exists between theoretically available P and various extractable P (5% significance level), which means that a proportional relationship exists between various extractable P and actually available P.

Difference between the amounts of various extractable P and theoretically available P varies. Water soluble P accounts only for 43% of theoretically available P, formic acid soluble P for 70% and citric acid soluble P for 80%, that is to say, the amount of available P determined through extraction by citric acid is the closest to the amount of theoretically available P. Consequently, we suggest that in formulating technical criteria for production of PAPR, the 2% citric acid extraction method should be used to determine available P in product.

Based on the above-described experiments and discussions, it can be held that conditions are available for China to develop PAPR. The most important significance in developing PAPR lies in enabling China to make full use of the moderate-and-low-graded phosphate rocks that account for about 80% of her P resources. It is just the reason that we carried out the research project. And it is for the same reason, too, that we are optimistic about the future of the development of PAPR in China.

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