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Foreword

I am indeed flattered to be given the privilege of writing the Foreword for this second edition of Pierre Becker's most successful volume on phosphoric acid. Since it appeared in 1983, the book has become the standard text for phosphoric acid, due not only to the expertise of Pierre, but also to the talented staff of helpers who, together, have amassed an amazing amount of useful data, such that the work becomes a virtual design manual.

The Foreword for the first edition was written by Philippe Moraillon, who referred to the progress made over the preceding 35 years. I like to think of myself as a bridge to a technology even further back than that, through my 25 years of association with William C. Weber and E. J. Roberts of the Dorr Company, later Dorr-Oliver.

Bill Weber and "Doc" Roberts were the principals in the successful development of the prototype for the "strong acid" dihydrate process, which still predominates today. The phosphate fertilizer industry in the late 1920s was just emerging from being based exclusively on normal super phosphate. The use of phosphoric acid to bind the new, cheaper synthetic ammonia was suggested in a 1930 article by Weber.

In 1931 the Dorr Company, which had supplied, worldwide, over the previous decade, fifteen or more phosphoric acid plants using the weak-acid, countercurrent decantation process, brought into operation a new phosphoric acid plant at Cominco's metallurgical facility at Trail, British Columbia, Canada. The design started out as a single-stage hemihydrate process. The filtration of the hemi slurry on internal drum filters, without the availability of synthetic fiber filtercloths, was unsatisfactory.

1.3 PHOSPHORIC ACID PRODUCTION: PARTICULARITIES OF THE WET PROCESS TECHNOLOGY

By its nature, wet process technology conserves most of the impurities found in the original phosphate ore, which are then included in the phosphoric acid produced. Consequently, the variety of the phosphate ores influences not only the process used but also the composition and characteristics of the phosphoric acid produced.

Wet process phosphoric acid technology, which will be described in the next sections, essentially comprises sulfuric acid attack and separation of the phosphoric acid produced from the calcium sulfate crystals resulting from the reaction. Both the attack and the separation, which is effected by filtration, are considerably affected by the nature of the ore and its impurities.

Besides calcium phosphate, the phosphate ores contain 10–15 major impurities and another 16 or so trace elements.* Organic matter, also present in many ores, is not included in this estimation. Each element contained in the ore has its individual transfer coefficient into product acid and waste solids.

Without enumerating all the effects on processes and economics due to the impurities, some of the more common are:

1. *Effect on crystallization:* The calcium sulfate qualities, due to the presence of the various impurities, affect filtration rates by a factor of 4 from one phosphate ore to another.
2. *Scaling:* Vessels and pipework are subject to deposits of various kinds. Heat transfer coefficients, pressure drop in pipework, are subject to heavy alterations.
3. *Sludge formation:* Some impurities are subject to delayed precipitation in the stored product acid or the final concentrated acid. These are sludges—a difficult problem for the phosphoric acid producer.
4. *Corrosion:* Despite the use of exotic alloys, pump impellers and agitator turbines can be subject to rapid deterioration by corrosion.
5. *Environmental aspects:* Acidic fluoride compounds evolve from reaction vessels and concentration plants. They have to be recovered and combined to produce salable or at least harmless compounds. Trace elements such as cadmium have aroused great concern, and in the case of specific phosphate rock sources, have affected their sales patterns considerably.

*Mainly heavy metals and rare earth elements.

Many impurities, despite tedious procedures, cannot be analyzed quantitatively with accuracy, either from the phosphate rock or from the phosphoric acid produced. For example, it is possible for a 15 to 25% absolute deviation in iron and aluminum contents, respectively, to be found within the same ore sample as measured by different laboratories.

If the problems listed above characterizing phosphoric acid wet process technology are not discouraging enough, consider, too, the complications from dust, foam, and so forth.

From the foregoing it is obvious that the science of phosphates and the technology of phosphoric acid is somewhat esoteric. Words such as "technology" or "calculation," in this case, have to be employed very carefully. Sometimes traditional calculation methods can be used and sometimes one has to rely on experience and accept a simple estimation based on similar cases.

An understanding of what and how to calculate in phosphoric acid technology is the objective of this book. We hope the reader will derive some advantage from the many years the various authors have spent in the dust and effluent gases of phosphoric acid plants, watching filter cakes and plugging pipes!

Like human beings, phosphates are fascinating; they never behave consistently. They like to be treated differently every time. Once you are married, even if only to phosphates, you need to use a fresh approach day by day.

1.4 HISTORY OF PHOSPHORIC ACID CHEMISTRY AND PRODUCTION USING THE WET PROCESS

The production of phosphoric acid by means of the wet process began to be developed intensively following World War II. As a simple transformation of calcium from a phosphate to a sulfate, the reaction is

$$(PO_4)_2Ca_3 + 3H_2SO_4 + 6H_2O \rightarrow 3SO_4Ca \cdot 2H_2O \downarrow + PO_4H_3 \qquad (1)$$

The reality is, in fact, not as simple because of the technology that must be used. The phosphate attack and the formation of the calcium sulfate take place on their own, so to speak, but the calcium sulfate crystals (gypsum or hemihydrate) then have to be separated from the phosphoric acid that is produced.

This separation must be thoroughly completed since, at the price of phosphoric acid, even a small loss at the filter will show up quickly in the economics of the operation. A properly functioning plant will, under normal running conditions, lose 0.5% of the acid during filtration. This percentage is increased by startups, and

should not exceed 1% (measured average of
liquid effluents that accompany the rejected
ɔt include the losses of combined P_2O_5 contained

the filter is achieved when crystallization at
This type of crystallization has not, however,
; several decades of work have been required.
:rystallization" in a phosphoric medium has been
ns of experimentation, which explains its long,
:ing phosphate with sulfuric acid, early pro-
conclude that great caution was necessary in
ıdustrial scale, for a number of reasons.
:ing very porous, reacts extremely quickly
ılfate crystals to grow in a regular manner.
xothermic, and the calories must be evacuated
; too hot, no more $SO_4Ca \cdot 2H_2O$ is created; but
hydrate or anhydrous material forms, which
.e filter. Also, if the reaction becomes too hot,
.ed in sulfate shells (coating) and the attacking
ıle losses of unattacked P_2O_5).
to work in a relatively diluted medium (27-30%
ses, 40-45% for most cases with hemihydrate
ving P_2O_5 concentration, viscosity increases
bits economical filtration. Mass transfer and
can be affected considerably.
ɔess phosphoric acid plants built between the
enerally produced between 25 and 50 tons of
roblems of mixing and agitation were poorly
ıe reactive media were not really homogeneous
'saturated. The poor crystals were therefore
g, an operation necessitating huge volumes of

one of these installations before it was de-
ıts were mixed in premixers fitted with great
ıg slowly and the reactions were completed in
ks. The gypsum was separated by decanting.
ɔperation meant that 700 m^3 was needed to
O_5 per day in the form of 25% acid by using
ıates available at that time. To reduce the
ation in the premixers, slurry was recycled
s been completed in a long series of reaction

lcium sulfate crystallization within media with
n of P_2O_5 has fascinated many researchers
30, Nordengreen took out patents for the manu-
ıtrated (40% P_2O_5) phosphoric acid by means

of the formation of hemihydrate or anhydrite ($CaSO_4 \cdot 0.5H_2O$, $CaSO_4$). Nevertheless, this process, like others, often ran into trouble on an industrial scale, and it was not until the 1970s that plants worked well with good yields from crystallizations other than calcium sulfate dihydrate.

It was the Japanese who after much research in this area managed to construct the first full-scale industrial units with an acceptable yield by filtering gypsum recrystallized from hemihydrate precipitated in the first stage. The idea of having purer gypsum for subsequent use was one of the main reasons for the development of this technique. Natural calcium sulfate, a rare mineral in Japan, is used in the production of cement.

In the 1960s there was a proliferation of hemihydrate-dihydrate processes (or vice versa), most of them involving double separation of the calcium sulfate. The economics of these processes have sometimes been dubious since a 2% recovery gain (U.S.$6 per ton of P_2O_5) and a few percentage points more concentration from plants which often produce a by-product steam that can be used for the phosphorice acid concentration process do not necessarily justify additional investment and increases in maintenance costs.

But difficult goals seem to create human incentives, and in spite of the great number of technical problems and a certain number of industrial failures with a consequent reconversion back to the dihydrate route, about 75 phosphoric acid plants among the total of about 320 plants in the world now work with nondihydrate routes. This is 23% of the total number of plants, but less than 20% of the capacity because most of them are medium-sized or small units. Most of these nondihydrate units, about one in two, use the Japanese Nissan process, a hemihydrate into dihydrate recrystallizing process with one filtration operation. A significant event should be mentioned here: a Dutch phosphoric acid producing company had two plants operating simultaneously, one a dihydrate and the other a hemihydrate single-stage process. In 1982 they decided, after considering their specific energy economics, to convert their dihydrate plant into a second hemihydrate operation.

In the field of dihydrate processing, the importance of mixing and agitation gradually improved and, toward the end of the 1960s, a French company developed a plant with a single reaction tank, demonstrating that rapid attack and good crystallization could take place together at the same time, provided that dispersion and the reactive volume were sufficient. The statistical age distribution of the crystals arriving at the filter did not seem to be as important as in the past.

The idea of a single reaction tank was very attractive to engineers, and even those who had believed in multitank operations brought these together in the form of compartments within a single shell while carrying on circulation by means of pumps. The new

single-tank reactors allowed their disciples plenty of scope to use their imagination, and extraordinary shapes were patented, ranging from egg-shaped to cigar-shaped. Of these, only the flat cylinder, the rectangular parallelepiped, and the egg have survived in any numbers. The others have more or less disappeared, being too large to find any room in a museum.

The evolution of stirring techniques can be gauged from the amounts of energy consumed per cubic meter in reaction as well as from the total volume in reaction compared to daily production. As late as the end of the 1950s, certain engineering firms were still proposing seven cubic meters of reaction volume per ton of P_2O_5 per day. Today it is common to recommend 1.5–1.8 m^3 for the dihydrate process, but some licensors operate with lower reaction capacities, estimating investment costs for reaction volume higher than those for increased filtration capacity. Although modern filtration equipment has been improved considerably during the current decade, the most economical investment ratio—reaction volume/filtration capacity—remains a case-by-case assessment.

More or less comparable dihydrate techniques have been developed in parallel in five geographical areas: Florida, Belgium, France, England, and Tunisia. Belgium and Florida developed the same process, the Prayon process, which accounts for the largest in size and the greatest number of dihydrate plants throughout the world (almost half of total phosphoric acid production). The Rhône-Poulenc process (Fig. 1.1) from France comes next with some 50 plants, followed by Jacobs Dorr (formerly Dorr-Oliver) with 27 plants. Next is SIAPE with its special design for low grade, foaming rock from Tunisia, followed by Fisons, England. A new process, the Gulf-Swenson isothermal process, appeared some years ago and is utilized by six plants.

During the late 1960s and the 1970s plant sizes increased and a 1000-metric ton P_2O_5 plant gradually became the standard size. But the increasing size of the production units brought with it problems associated with the relative decrease in surface area. Cooling, which was previously carried out by bubbling with air boxes (a crude system that should not be allowed outside the laboratory, if at all), is a function of the surface area of the slurry. The system demands a lot of energy (large volumes of air have to be forced through the slurry) and the resultant thermal exchange is poor. Consequently, it was necessary to discharge large volumes of polluted air (70,000 m^3/hr for every 100 tons of P_2O_5 per day.

At the same time, still using air circulation, ways were developed to get rid of the calories by spraying the slurry through the air, which is more economical of energy. Nevertheless, cooling still needs a certain amount of air and, in the reactor, the necessary surface area-to-volume ratio tends to bring large plants close to the geometric norms of Camembert cheese.

FIG. 1.1 World's largest phosphoric acid plant (8 × 600 tons/day P_2O_5), Rhône-Poulenc process at Djorf Lasfar, Morocco. (Courtesy of Office Cherifien des Phosphates, Morocco.)

Vacuum cooling, in which the slurry is pumped into a vacuum chamber, where evaporation (whence the cooling) is instantaneous and not related to the surface area of the reactor, allows systems to be enlarged more easily. However, it is more expensive, and large quantities of polluted cooling water are extracted instead of air.

Filtration has improved greatly thanks to improvements in filters, which can be sized to suit production capacities of 1200–1800 tons of P_2O_5 per day and even more with new projected filter sizes. Counterflow washings with hot water being recycled one or two times produce very good filtration recoveries. The appearance of plastic materials in the 1960s meant that one could replace stainless steel tubing and separators, thereby reducing capital and maintenance costs.

Filter speeds are now higher and, since the specific rate of filtration increases with the speed of revolution of the filter, it has been possible to increase substantially the number of tons filtered per square meter of effective filtration area. A filter revolving at one revolution every 4 min will filter 1.4 times more per square meter than a filter turning once every 8 min.

This fact, combined with improvements in filter cloth, means that it is now easy to produce 7 tons of P_2O_5 per square meter (at a speed of one filter revolution every 4 min) with a Florida phosphate, and with a filtration recovery greater than 99%, whereas 20 years ago this figure would have seemed a daydream in spite of the quality of phosphates, which was then quite superior.

Current developments deviate slightly from the direction that phosphoric acid techniques had long been following. This is due to the appearance of poorer quality raw materials. As a result of price increases, numerous deposits which were known but not previously exploited for reasons of quality or profitability are now supplying increasing tonnages, mostly in national markets. As a result, new plants have to be simple, robust (often the new minerals are more corrosive), and easy to operate (the local farmer should be able to operate them after suitable retraining).

These new developments have given added impetus to the dihydrate process which 15 years ago was thought to be doomed to slow extinction because of more elaborate processes. Today even with exotic newcomers appearing in the phosphate rock world market, it is still a reliable process capable of guaranteeing economical production of phosphoric acid.

1.5 RAW MATERIALS FOR WET PROCESS PHOSPHORIC ACID PRODUCTION

1.5.1 Commercial Phosphate Rocks: Technology and Economics

World Phosphate Rock Production and Resources

In 1986 the world's phosphate rock production was estimated to be 142 million tons of commercial ore. There are some 200 minerals containing more than 1% P_2O_5, but the most important for the phosphoric acid industry is the apatite group [5]:

$$(Ca, Na_2, Mg)_{10}(PO_4)_6{}_x(CO_3)_x F_y(F, OH)^*_{2\,y}$$

If mined at 1975 prices, the world reserves of commercial-grade phosphate rock would be 117,000 million metric tons.† Consequently, the current growth rate for phosphate rock production should not be limited by considerations for scarce ore deposits.

As mentioned previously, there are two main types of apatite deposits: sedimentary and igneous. Sedimentary deposits are the most important for phosphate rock production; about 85% [6] of the

*With y = (0.33x to 0.5x).
†Based on data from the U.S. Bureau of Mines.

present world production is of that origin. Both sedimentary and igneous phosphate ores are associated with a large number of impurities.

Sedimentary rocks exhibit a wide range of chemical composition because of the various types of associated gangues. As compared with igneous ore, sedimentary rocks contain more carbonates and fluorides and usually more iron and aluminum. They present as a porous material and offer a large surface for chemical reaction. Most of the time they contain organics, which are responsible for the consequent coloring and foaming that occurs in the acid and finished products.

The largest sedimentary rock mining areas are in Florida and Morocco, both areas producing together about 60 million tons of commercial rock. Igneous rocks are produced in the USSR (Kola), South Africa, Brazil, and Finland.

Mining and Beneficiation

To bring a phosphate rock onto the international market, the ore has to be mined, concentrated, and transported to the nearest port, from where it is shipped to a phosphoric acid plant or some other type of phosphate-consuming industry. Minability of a deposit from an economic point of view is possible when the sum of the costs of these operations fits the current economics of the phosphate industry and when the phosphate rock meets a certain number of quality standards.

Mining is done by either open cast mining or underground mining. Open cast mining (Figs. 1.2 and 1.3) consists of removing the overburden covering the phosphate bed and recovering the ore by mechanical shovels or by hydraulic methods. The economics of open cast mining depend essentially on the thickness of the overburden layer and the ore bed as well as the yield of recovery of the P_2O_5 contained in the mined ore bed.

Economic conditions can allow up to 1.5–2 m^3 of material to be removed per ton of reclaimed ore. When the overburden is too large, underground mining has to be chosen, which has been done, for example, in Tunisia, (Figs. 1.4 and 1.5), Jordan, and Egypt, and for the igneous Kola rock in the USSR.

Beneficiation or upgrading of the phosphate ore has called for a number of different techniques. In favorable cases, to reach commercial grades of some 30% of P_2O_5, only screening and drying is necessitated (e.g., in Morocco, Nauru, and Christmas Island). However, in most cases the ore quality needs removal of some by-product impurities. For sedimentary rock, suitable techniques for economic ore concentration are: crushing and screening or grinding, followed by pneumatic particle size selection and washing and desliming by hydrocyclones or classifiers. These techniques are based on particle size selection. The phosphate ore particles usually occur within particle size ranges between 60–80 μm and 1000–1400 μm.

TABLE 1.11 World Production of Commercial Phosphate Ore Concentrate by Countries (Thousands of Metric Tons)

Country	1980	1984	1986
Algeria	1,025.4	1,000.2	1,203.3
Australia	-	14.5	34.3
Brazil	2,921.3	3,854.9	4,508.8
China	10,726.0	14,210.0	9,500.0
Christmas Islands	1,713.3	1,258.6	825.0
Colombia	5.3	28.1	27.2
Egypt	658.3	1,043.4	1,271.5
Finland	124.8	477.3	527.0
India	427.2	759.2	750.0
Iraq		1,500.0	2,000.0
Israel	2,610.5	3,312.3	3,673.2
Jordan	4,242.7	6,263.1	6,249.2
Korea, Dem. Rep.	500.0	500.0	500.0
Mexico	330.0	374.9	600.0
Morocco	18,824.2	21,244.9	21,177.9
Nauru Island	2,086.7	1,358.5	1,493.6
Pakistan	-	-	50.0
Peru	13.9	12.7	5.2
Senegal	1,459.0	1,873.5	1,850.5
South Africa	3,282.0	2,564.1	2,922.5
Sri Lanka	-	16.0	15.0
Sweden	-	127.6	191.5
Syria	1,319.4	1,514.0	1,606.0
Tanzania	-	14.5	10.0
Togo	2,932.8	2,695.6	2,313.9
Tunisia	4,581.9	5,345.9	5,950.6
Turkey	21.3	95.6	2.7
USSR	24,668.3	32,900.0	33,200.0

TABLE 1.11 (continued)

Country	1980	1984
U.S.	53,362.8	47,145.
Venezuela	-	-
Vietnam, Dem. Rep.	400.0	200.
Zimbabwe	-	125.
Other	213.3	-
World total	138,450.4	151,829.

1.5.2 Sulfur

Beside phosphate rock, sulfur by means of sulfuricl i: second raw material needed for phosphoric acid proion process phosphoric acid is the major world sulfur cme nearly 50% of the total production. Sulfur is produfr stone (37 million tons per year as S), pyrites (11.4io and other forms (9.1 million tons of S).

The world sulfur production and prices have beul strong variations well before the price cycles of phate fertilizers (see Table 1 in Appendix B). The price th "sulfur-in-all-forms" production are, consequently, ng phosphoric acid economics. Roughly 0.8-1 ton of sr i to produce 1 equivalent ton of P_2O_5 by the wet pro. demand have been estimated to balance closely; eve, t phate fertilizer growth rate is expected to be rathenin next 5 years. However, it is not to be expected thigl prices will last for a longer period because phosphært production economics would then avoid expensive su cc in one or more of several ways:

Use pyrites or waste smelter sulfuric acid.
Use partial acidulation or ground rock fertilizers.
Use nitric acid instead of sulfuric acid.
Recycle calcium sulfate to manufacture H_2SO_4.

Table 1.12 indicates world sulfur production bygr areas.

severely, whereas the state-backed Moroccan and Jordanian mine integrated phosphoric acid industry, for example, can expect an improved supplier position following the present era of over capacity (because a large number of plants in Europe and the United States have been shut down).

1.6.2 The Era of the Great Overturns

Looking at the world's regional phosphoric acid production and consumption throughout the past decade, we can see dramatic changes. Whereas the U.S. phosphate industry declined nearly 20%, countries like Morocco, Tunisia, and Jordan have expanded their capacities considerably. The phosphoric acid plant in Djorf Lasfar, Morocco (Fig. 1.1), is, to date, the largest phosphoric acid plant in the world. Former importing countries, such as Brazil and the Philippines, now produce their own phosphate fertilizers.

Industrial phosphates, also produced predominantly in developed countries, cannot register better results. Their progress is stalled primarily by environmental problems. Detergent manufacturers, the larger users of industrial phosphates, are said to be responsible for river and lake eutrophication. The total consumption of industrial phosphates is expected to show a nearly zero growth rate (see Tables 1.13 and 1.14).

TABLE 1.13 Industrial Phosphate Consumption Trends in the United States (Metric Tons per Year)

	1984	1989 (expected)
Detergent builders and water treatment	167,400	163,300
Food and beverages	29,100	32,100
Toothpaste	2,700	2,700
Metal finishing	12,700	12,700
Others	115,500	118,500
Exports	24,000	24,000
Total	351,400	353,300

Source: *Chemical Week*, Mar. 19, 1986.

TABLE 1.14 Industrial Phosphate Market by Region and End Use, 1987 (Thousands of Tons of P_2O_5)

	Soaps, detergents, cleaners	Food	Water treatment	Others	Total
Western Europe	437	36	22	60	555
Eastern Europe	233	13	13	18	277
North America	342	72	64	85	563
Africa	76	5	2	4	87
Latin America	207	13	10	10	240
Asia and Oceania	275	14	11	13	313
Total	1570	153	122	190	2035

Source: World Bank.

1.6.3 World's P_2O_5 Demand Expectations: Key Factors

The forecasts made during the past decade have all proved overestimates. The present careful projections, 2.3–2.5% P_2O_5 demand growth per year [8, 9], may be heavily influenced by the disappointing results of previous forecasts.

There are too many key factors working in opposite directions to make completely dependable forecasts. The key factors are as follows:

Factors in Favor of Improving the Market Situation

Phosphate rock mining overcapacity
Large developing countries with high population densities at the threshold of high agricultural and industrial growth rates, for example, India and China
Increasing availability of sulfuric smelter acid as a raw material for phosphoric acid
U.S. currency rate
Plant shutdowns

Market-Depressing Factors

Low food prices
High farming yields

Environmental concerns
~~Calcium sulfate disposal concerns~~
High sulfur prices

Comments to Key Factors

Phosphate Rock Overcapacity. This was discussed before (Section 1.6.1 and Fig. 1.7).

Developing Countries. India and China both have enormous consumption needs, as can be seen from Table 1.15. India has registered an 8% average growth rate for P_2O_5 consumption during the past 10 years. Its scarce reserves of domestic raw material will keep the country a large P_2O_5 importer. The 1985-1986 consumption rate of 2.06 million tons of P_2O_5 is expected to expand to 3.4 million tons in 1991-1992 [10]. China's need for phosphate fertilizers is even larger. Chinese experts estimate that 9 million tons of P_2O_5 will be used in 2000 [11]. However, there are transportation and infrastructure problems; changes in management, knowledge, and habits; and financial needs to be considered. Consequently, it can be assumed that the medium term growth rate of fertilizer use in China will probably not be as high as in India. Table 1.16 shows some key figures for China. Whereas the main nitrogen fertilizer still used in China is ammonium bicarbonate, fused phosphates and single superphosphates are the main phosphatic fertilizers. To date, very little phosphoric acid has been produced in China, and it represents only a few percent of the total consumption.

It is very likely that China will have to import phosphoric acid and phosphatic fertilizers in large amounts before domestic mining and industry will take over the large demand. Current needs are estimated at 2 million tons of P_2O_5 in excess of actual consumption. However, imports will have to be met by the availability of foreign currencies or commodities.

Smelter Acid Availability. Increasing supplies of smelter acid will be available in the near future. In 1986, 7.3 million tons were available, but Chile, Mexico, Australia, Canada, the Dominican Republic, and others will come on line with large additional tonnages, so that in 1993 the tonnage should exceed 12 millions. The use of cheap smelter acid instead of expensive sulfur will be essentially a problem of logistics [7,13].

U.S. Currency Rate. International prices for phosphates and phosphatic fertilizer are rated in U.S. dollars. Large buyers such as India will have their purchasing power improved by a low U.S. dollar exchange rate.

TABLE 1.15 Key Figures and P_2O_5 Consumption for Various Countries

	Farmland (millions of hectares)	Population 1986 (millions)	Phosphate fertilizer consumption (millions of tons P_2O_5)	Application rate (kg P_2O_5/ha)	GNP per capita (U.S.$/year)	Growth rate (GNP%/yr)	Population per hectare farmland
India	173	760	2.06	10.3	260	1.8	4.39
China	360	1050	2.66	7.4	—	—	2.92
U.S.	140	235	3.7	23.4	14,000	1.5	1.68
France	30	54	1.6	53.3	11,540	2.2	1.80
Brazil	70	130	3	—	2,170	2.8	1.86
Australia	—	15	0.4	—	11,000	0.9	—

Figures

1975	1980	1984
0.920	0.983	1.036
150	182	192
4.85	7.64	8.17
0.30	0.23	0.26
1.53	2.31	2.36
0.027	0.41	0.30
374	366	360
23%	15.5%	9.12%
196	301	375

s very difficult to forecast the number of
xpected; there may be more than has been

fortunately, farmers and the fertilizer
with low food prices for a number of years.
ulation densities and low per capita income
ese), governments will back a policy of
mers are easier to control than are hungry
an areas, so there is little hope for change.

Continued worldwide improvements in
bined with a decreased rate of world con-
normous corn, rice, and grain stocks,
crop prices.

s. Environmental concerns will affect both
on capacities and have already severely
ite consumption in a number of developed

countries. Involved primarily is sodium tripolyphosphate (STPP), a principal component in washing powders. A number of European countries have, by decree, limited STPP levels in detergent formulations (e.g., Norway, Sweden, West Germany, Finland, Italy, Austria). Some jurisdictions have even banned STPP [e.g., Switzerland and a number of western states in the United States (where regulations are carried out at the state rather than the federal level)]. STPP is said to be responsible for the eutrophication of rivers and lakes to which it is carried in wastewaters. Some developed countries, having traditionally used high fertilizer application rates, have raised soil protection laws and have set phosphate soil concentration limits and special use taxes (e.g., Netherlands, Denmark).

Another environmental concern is cadmium, contained in most phosphate ores. Cadmium is difficult and expensive to remove from phosphoric acid (see Section 9.5.1). Because of cadmium, the Dutch phosphoric acid industry is currently fighting for its life against environmentally concerned government authorities.

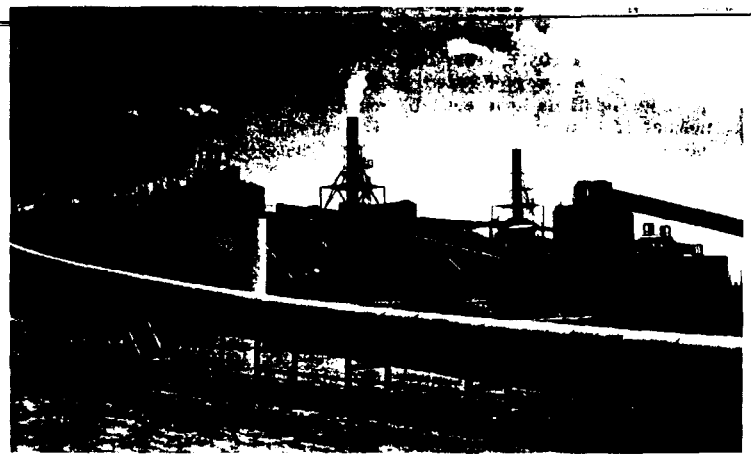
Calcium Sulfate Disposal. The problem of large calcium sulfate waste disposal connected to phosphoric wet process acid production has forced a number of plants located in highly populated areas to reduce their capacities. This problem is of more concern in developed countries than in others. Morocco, for example, does not seem to suffer from environmentalistic pressures despite sending some 30,000 tons of gypsum per day into the ocean.

High Sulfur Prices. Sulfur costs often outweigh phosphate raw material costs. Depending on the phosphate rock composition, 0.8–1 ton of sulfur is consumed per ton of P_2O_5 produced. The sulfur producers seem to maintain a world sulfur shortage, letting the situation improve from time to time to discourage the development of alternative sources.

Price peaks occurred during the 1950s and 1960s, and prices skyrocked in 1980, after which they have stayed at a high level (see Appendix B, Table B.1). (Peaks of U.S.$170/ton were registered in 1985–1986.) Severe shortages were announced in 1986. Currently, prices are declining.

1.6.4 Conclusions

The unexpected current world market situation in the phosphate industry has not discouraged forecasting activities; in fact, there never was so much. Most forecasters predict low growth rates, typically 2.3–2.5% per year. The most pessimistic [14] predicts a 2.0% rate. Whatever the growth rate, strong competition between mine-integrated, government-backed industries in developing countries and environmentally burdened (often private) producers in developed



(a)

(b)

FIG. 1.8 Modern superphosphoric acid plant of capacity 1200 mt/day P_2O_5 at La Skirra, Tunisia, completed in 1988. (a) Two acid units, (b) pipeline to harbor.

countries has initiated a nonreversible trend to move the phosphate industry toward rock sources located in areas with fewer economical and environmental constraints. Ironically, the developed countries' production units have the advantage of more modern, better performing equipment (Fig. 1.8). Furthermore, most rock producers, now phosphoric acid producers, will try to maintain a high rock price policy to enhance the trend.

Such competition will hardly permit the survival of companies without assets. For those who do not have any raw material at their disposal, only high technology and associated alternate products can strengthen their position. Sulfuric acid should be used twice (with phosphoric acid as an end use), and waste products should be processed into marketable products. Energy should be saved throughout the plant. This may not always be easy or even feasible, but if there is no other alternative, we have to try. Some producers have already done it nicely.

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circulation and installed before the filter, is supposed to give an additional margin of error to the total retention time of the phosphate particles.

Generally speaking, reaction volumes correspond to ratios of 1.5–2.5 m^3/ton of P_2O_5 produced per day. However, by "pushing" production, plants can sometimes be found working at a ratio of less than 1 m^3/ton of P_2O_5 produced per day.

Since crystallization is often spread unevenly among the various tanks or reaction sections, precipitation rates per cubic meter are sometimes very high. In older premixer tanks figures of more than 1 ton of $SO_4Ca \cdot 2H_2O$ per cubic meter were common, whereas modern single tank units work at about 0.09–0.180 ton of gypsum per cubic meter per hour.

The cooling necessary to maintain a temperature of 70–80°C in the reactor and 70–75°C at the filter is provided either by a cooling airflow or by a vacuum cooling system of pumped slurry cycle. Air cooling is based on various ratios according to the technology involved: 30,000–70,000 m^3/hr per 100 tons of P_2O_5 per day (30,000 m^3 is low, while 70,000 m^3 is far too high).

Vacuum coolers work at various slurry flow rates, which calls for a different temperature difference in each case. In practice Δt is between 2 and 10°C. Cooling system scaling problems are obviously greater with 10°C than with 2°C.

Filtration Section

Filtration, too, is subject to a large variety of flow ratios according to the nature of the process, but above all it is a function of phosphate quality. The use of additives (flocculants) can sometimes improve these values. Poor phosphates operate at around 2 tons of P_2O_5 per day per square meter of filtration area; the most common, commercial phosphates, 4–5 tons; good ones, 7 tons, and the best, about 9 or even 10 tons of P_2O_5 per day per square meter of effective filtration section area.

All these values are expressed on a base for filters working at a filtration cycle time of 4 min with a washing yield of P_2O_5 recovery over 99% with 28–30% acid. Faster filters improve on these figures, and slower ones lower them.

Three filter types are currently used for wet process phosphoric acid production: belt filters, pan filters, and table filters. The largest single filter can to date achieve production rates up to 1800 metric tons of P_2O_5 per day (see Chapter 6).

The recycled acid flow varies as a function of the P_2O_5/CaO ratio in the phosphate. The lower this ratio, the more P_2O_5 has to be recycled to keep the slurry composition within the necessary standards. In Fig. 2.1, with low-grade rock, recycled P_2O_5/produced P_2O_5

ratio is 1.64, whereas it is only 0.98 with high grade rock (Fig. 2.2) (see also Section 3.2). This is one of the most important factors to consider when assessing a new rock versus the adapted process technology.

High recycle P_2O_5 rates endanger some technologies, such as wet grinding or high-strength acid processes. Whereas the yield following recovery with wet grinding of the high grade rock (Fig. 2.2) would still be over 95%, the low grade rock (Fig. 2.3) would drop from 95.4% recovery to 94%, because of reduced cake wash flow.

Product acid resulting from dihydrate operations currently yields 27–30% P_2O_5. However, it can be lower when very low grade rock is consumed. Calcium sulfate resulting from the reaction is calcium sulfate dihydrate, which is for most cases wasted to piles or sent into bodies of moving water. Environmentally safe recycling into useful products is under investigation.

2.1.2 Nondihydrate Processes (Hemihydrate Processes)

State of the Art, 1987

Traditionally, phosphoric acid has been produced under reaction conditions of 28–32% P_2O_5 and temperatures of 70–80°C, the calcium sulfate being essentially precipitated as dihydrate. Local requirements in Japan caused the need for modification of this technique, and some low-strength hemihydrate recrystallization processes were developed that produced a high-quality calcium sulfate for gypsum board manufacture. These processes were still limited to approximately 30–35% P_2O_5 in the product acid.

More recently, in a number of cases of differing local requirements, the incentive to produce an acid of high strength (40–50% P_2O_5) without the use of steam has caused a number of companies to accept the challenge of high-strength hemihydrate technology. If the cost of oil and power were again to increase, the economic advantages of production of higher-strength acid without the use of steam would once more be of greater interest.

Since the publication of the first edition of this book there has been a general tendency to reduce acid strength in the high-strength processes from 50% to 42–45% P_2O_5 (this is probably due to higher values for the P_2O_5/energy ratio), but this intermediate strength can easily be obtained without the use of steam by hot water loop concentration (by evaporation) of the dihydrate product acid. (The hot water is obtained from sulfuric acid intermediate absorption heat recovery via heat exchanger systems [3–18] (see also Section 7.1.1). In fact, when considering revamps, the conversion from dihydrate to hemidihydrate requires a large investment *and* considerable space. In many cases the lower investment, low space requirement, and low

risk of hot water evaporation of dihydrate acid may well be much more interesting than the novel high strength phosphoric acid technologies.

The industrial experience gained from the increasing number of operating plants should enable prospective purchasers of this type of technology to have a chance to evaluate the real savings of each process, thus enabling them to evaluate the overall performance of this type of process, whereas previously they could obtain only the claims made by the process licensors.

The growth of high strength processes has been somewhat slow during the last five years, but this can easily be justified, as the overall growth rate in the industry has been very small; also, the price of oil has decreased very markedly and has up to now shown little signs of increasing, at least in the medium term.

Hemihydrate processes do require a high level of technical and operational expertise in order to avoid unwanted transformation of the semistable hemihydrate into dihydrate. Nevertheless, in certain cases the operation of a single stage hemihydrate process can sometimes be simpler than the respective dihydrate plant, due mainly to the possible absence of grinding, evaporation, and storage sections. Conversely, two stage hemihydrate/dihydrate processes with recrystallization and double filtration can be more difficult to operate than the equivalent dihydrate process.

Utilization of the reaction/filtration system of a single stage plant is normally about 85–95% of available operating time. This excludes one 2 week or two 1 week shutdowns. Thus the operating time is from 298 to 333 days/year. There is a large variation due to standards of maintenance, proximity of suppliers, and the scaling/corrosion tendencies of each phosphate. It is well known that whatever the process or product, the longer the process train (number of items of equipment without intermediate buffer storage), the lower the utilization factor. Thus any processes with two filtration stages can expect utilization of only about 80–90%, or 289–316 days/year. Thus the plant size of any two stage process will need to be about 5% greater in instantaneous capacity to give the same annual production rate as a single stage plant.

How significant capital cost is compared with other costs, such as raw materials, utilities, maintenance, and labor, has to be fully evaluated in each case, but in many cases the raw material costs are heavily weighted in the overall production cost.

Hemihydrate Processes Available

Process Routes [19–29]. In order to compare the many hemihydrate processes and dihydrate processes, it has been necessary to classify them into five "process routes." This generalization, although aiding evaluation, does not account for the specific advantages or disadvantages of each process as to plant performance,

process, or engineering considerations. This treatment is intended only as a preliminary guide; the advantages or disadvantages quoted should be confirmed by discussions with each process licensor.

Each process route is defined by the process philosophy, including attack conditions and number of filtration stages. It is not intended to imply that all processes within each process route perform in the same manner. However, the physical chemistry is essentially the same, and differences in product and by product quality and raw material consumption should in general be small for a given phosphate.

The five basic process routes are designated as follows:

1. *DH (dihydrate)*: conventional dihydrate process, either single or multitank, normally producing acid 28–30% P_2O_5 (e.g., Prayon, Norsk Hydro DH, Siape, Rhone Poulenc, Gulf Swenson, Jacobs Dorr, and others)
2. *HRC (hemidihydrate recrystallization)*: single filtration stage; reaction in hemihydrate regime followed by recrystallization to dihydrate and filtration to produce 30–32% P_2O_5 acid (e.g., Nissan H, NKK [30–39])
3. *DH/HH (dihemihydrate)*: reaction as dihydrate at a slightly higher strength (32–35% P_2O_5); separation of product acid without cake washing; conversion to hemihydrate and countercurrent washing of hemihydrate cake (e.g., Central-Prayon [40–45])
4. *HH (hemihydrate)*: single-stage hemihydrate process producing 40–48% P_2O_5 acid directly from the filter (e.g., Norsk Hydro HH, Oxy Hemihydrate, and Prayon PH11 [46–61])
5. *HDH (hemidihydrate)*: reaction in hemihydrate regime, filtration to produce 40–52% P_2O_5 acid; washing and repulping of hemihydrate cake in recrystallization tank; conversion to dihydrate with the liberation of the lattice loss and the filtration of the dihydrate cake (e.g., Norsk Hydro HDH, Nissan C, Prayon PH2, Oxy-Recrystallization, Jacobs HYS [62–86])

Typical block flowsheets outlining process steps are shown in Fig. 2.4. A comparison of the technologies available tabulated by process route is presented in Table 2.1. The advantages and disadvantages of each process route are listed in Table 2.2.

Case Studies. Every production unit for phosphoric acid has its own requirements regarding raw materials, utilities, product quality, and by product quality. The five process routes can be classified into four specific cases in terms of these characteristics.

1. *Weak acid: impure gypsum; process route: dihydrate.* Under these restraints the proven dihydrate processes are normally still superior, even with increasing power costs, provided that steam is available for evaporation. Process modifications have enabled

Maintenance Costs and On Line Time. Maintenance costs vary with the capital cost, local conditions, corrosion rates, and materials of construction.

The hemihydrate processes have a relatively low capital cost, and even though the materials of construction are more sophisticated and corrosion rates are often higher, this type of plant normally has a lower maintenance cost than that of a dihydrate plant if rock grinding and concentration are included in the latter.

The HDH processes have a higher level of investment. The first stage requires the same maintenance as a hemihydrate plant. The second stage is relatively simple and increases maintenance costs only marginally. The on-line time of these two hemihydrate processes depends on the phosphate source, its scaling and corrosion properties, and local conditions.

One of the major fears of production people without experience in hemihydrate processes is related to the filtration of hemihydrate slurries and the possibility of conversion on the filter. Igneous phosphates have a relatively low transformation rate, and no such problems were encountered on Kola phosphate in the Jacobs/Dorr HYS process. Norsk Hydro patented a conversion retarder for use when processing sedimentary phosphates (Togo, Morocco, Florida), and this is dosed at a controlled rate into various parts of the filter circuit. Oxy uses an additive during the attack and crystallization stages of their process to maintain a low level of supersaturation, and this seems to prevent hydration on the filter with their northern Florida phosphate. Prayon complexes the free fluorine level by additives to reduce corrosion and to create stable hemihydrate. The results of these industrially proven units show that filtration can be effected in such a way to avoid problems of conversion to dihydrate on the filter. In fact, one unit operating on Togo phosphate has virtually no scaling in the filter circuit, and in fact requires less frequent filter wash cycles than those of a dihydrate plant using the same phosphate.

The selection of a filter for hemihydrate filtration is a critical factor for the success of any project with this requirement [87]. For the early Central Prayon plants, the original Prayon tilting pan filter was highly modified with internal wash and prewash features, thus enabling a high on line factor to be obtained on the filtration of the hemihydrate slurry [46]. This know how was incorporated into the Bird Prayon unit supplied to the Nissan unit at Petrokemia Gresik in Indonesia, which operates satisfactorily.

The first Ucego used for hemihydrate filtration also required modifications to allow for an increased expansion due to higher slurry temperatures to create better cloth washing and to ease the descaling of the pipes connecting the cells to the central filtrate distributor.

Belt filters (Delfilt, Prayon Eimco, Philippe) may well be a good solution to the problems of hemihydrate filtration, the major drawbacks

being the size and belt life limitations. In severe cases of high temperature and high sulfate content, the belt life can be less than 5 years. Apart from this, attention to detailed process design can enalbe a high-reliability filter to be manufactured. Excellent cloth and belt washing enable scaling to be minimized or even prevented.

As with dihydrate processes, the filter wash cycle does depend on the phosphate. Both Norsk Hydro and Nissan have noted fluosilicate scale deposition with some phosphates in the strong wash sections of the hemihydrate filter [64,68,74], and both of them claim to have been able to reduce this by process modifications. The extent of this problem seems to depend on the impurity levels in each phosphate, as the Windmill plant when operating on Togo had no such problems, and Occidental has stated that they do not have this problem in their plants, which both operate on northern Florida phosphate. Physical chemistry suggests that this problem should be largely independent of process.

Corrosion also affects on line time, and this, too, depends on phosphate quality. Until 1980,* Togo phosphate contained as much as 1000 ppm chloride in the 37% P_2O_5 concentrate, but could be processed successfully using alloys such as Uranus B6, Sandvik 2RK65, or 904L for the wetted parts of slurry pumps, resulting in a reasonably long life. However, in some cases it has been necessary to use Saniero 28 for pumps and agitators.

Overall the effect of maintenance costs on overall production cost is small and depends largely on the phosphate, not the process. The on line time of two-stage processes does tend to be lower than that of the single-stage processes, and installed capacity will need to be about 5% greater to obtain the same annual production rate. However, as the capital cost is often not very significant in the overall production cost, this fact has little effect on economics *provided that* allowance is made during the selection of plant capacities, or else it could cause problems within the overall fertilizer complex.

Raw Material Costs.

Phosphate. Coarse phosphate can be fed directly to a plant, but this does not necessarily mean that a grinding unit is not required. For example, Florida pebble could not be fed directly. If grinding is required, wet rock grinding cannot be used, as it is not acceptable in terms of the water balance. The low efficiency of the HH processes increases the consumption of phosphate, while the high efficiency of the HDH processes decreases consumption compared with DH processes. If high strength acid (48% or more P_2O_5) is to be

*After 1980 a dechlorination system for Togo rock was installed to reduce the chlorine concentration in rock to 500 ppm.

produced in a HH process, the phosphate feed must be dry to allow ample cake wash water, but the HDH process can accept a moist feed (up to 10% H_2O) due to the extra 1½ moles of water of crystallization. Oxy is at present producing 42% acid in their HH unit using a moist phosphate. Slurry feed cannot be tolerated by either process route while still producing strong acid.

Igneous phosphates do have a tendency to be more difficult to recrystallize from hemihydrate to dihydrate (see Section 2.2.5, "Hemihydrate and Dihydrate"). Nissan, in its low strength H process (HRC mode), claims to have overcome this problem in the case of Kola phosphate by operating at lower sulfate levels during recrystallization. The Dorr HYS process did not operate satisfactorily on Kola due to low levels of recrystallization, but progressively, the effect of impurities and process conditions on conversion should become better defined, and it is possible that this limitation may well be overcome. In single stage hemihydrate processes igneous phosphates perform well, as proven by the number of Soviet plants operating on Kola phosphates in the hemihydrate mode.

Sulfuric Acid. Due to the lower sulfate/P_2O_5 ratio in the product acit, the high strength process shows a saving in sulfuric acid consumption over that of dihydrate processes at the same efficiency. In fact, the HH processes show a saving even when their efficiency is as much as 3.5% lower than the DH processes. Further savings may apply in specific cases due to changes in cake impurities, but this depends on the phosphate source.

The HDH processes have the lowest sulfuric acid consumption levels of all processes, due to the very high efficiency and an acid quality similar to that of the HH processes in terms of sulfate/P_2O_5 ratio. Typical figures for sulfuric acid soncumption at various efficiencies for the three processes (DH, HH, and HDH) are shown in Fig. 2.18.

Sulfuric acid added to the hydration tank in a HDH process, replacing the lattice loss of the hemihydrate, effectively increases recovery and reduces the overall sulfuric acid consumption per ton of P_2O_5 produced. The loss of sulfuric acid together with the water-soluble P_2O_5 is slightly higher than in the DH process, due to the higher SO_4/P_2O_5 ratio in the hydration tank, but this is not significant overall.

Additives. The high strength processes often require additives to control reaction, crystallization, and recrystallization conditions. Defoamer is often required to control "gassing" in the case of phosphates with high organic and CO_2 contents. The stronger acid is more viscous than the equivalent DH acid even though it is normally 90-100°C rather than the 70-80°C of DH units. Oxy also uses a premix tank to reduce gassing in their draft tube reactor.

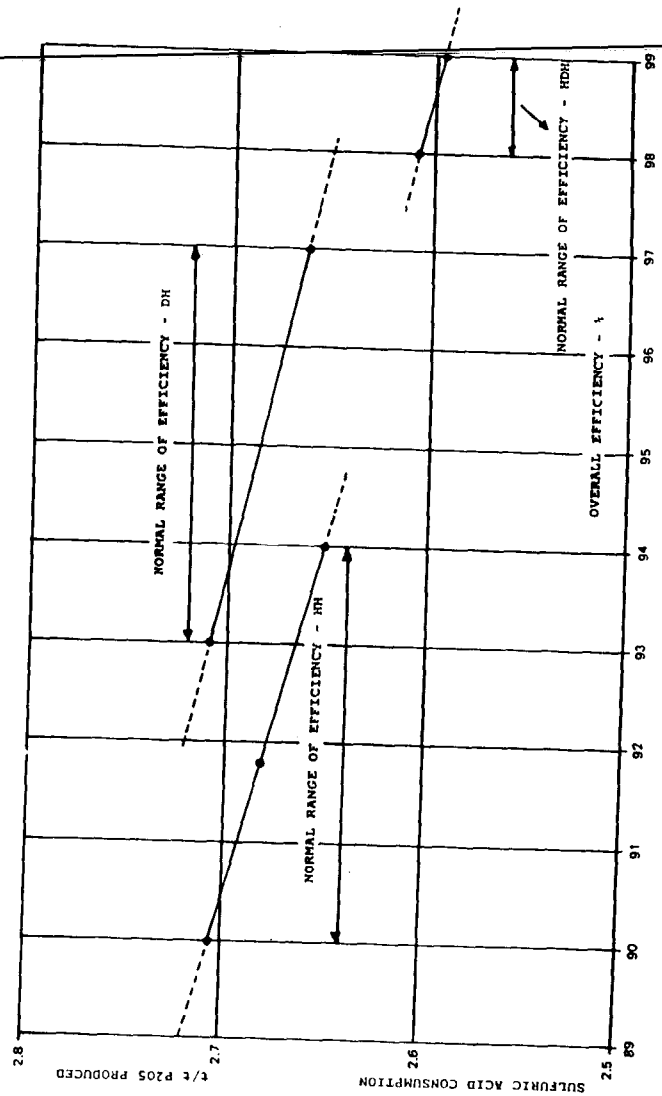

FIG. 2.18 Sulfuric acid consumption versus overall efficiency of DH, HH, and HDH processes.

TABLE 2.4 Solubilities of $CaSO_4$ Hydrates in Phosphoric Acid According to Taperova and Shulgina (wt %)

Acid concentration (wt % P_2O_5)	Temperature (°C) 25 DH	25 HH	40 DH	40 HH	60 DH	60 HH	80 DH	80 HH	90 DH	90 HH
5	0.50					–	0.85	–	–	–
15	0.70		–	–		–	1.4	–	–	–
25	0.70		–	–	–	1.5	1.45	–	–	–
30	0.60	1.05	0.8	–	1.0	1.25	1.35	1.38		1.4
35	0.45	0.85	0.65	0.9	0.9	1.0	1.25	1.15	–	1.2
40	0.40	0.6	0.55	0.7	0.75	0.80	1.05	0.9	–	0.95
45	0.30	0.4	0.5	0.5	0.65	0.6	0.9	–	–	0.75
50	0.25	0.2	0.4	0.4	0.55	0.4	–	–	–	0.5

Source: Ref. 1.

2.2 REACTION AND CRYSTALLIZATION

The objective of this section is not to describe different wet process phosphoric acid systems, but to analyze in detail the different chemical phases of phosphoric acid production. These different phases occur within the various acid processes, whether calcium sulfate is crystallized as dihydrate or in another form.

Phosphoric acid is produced by reacting sulfuric acid with naturally occurring phosphate rock. The reaction combines calcium from the phosphate rock with sulfate from sulfuric acid, and the resulting calcium sulfate is separated from the reaction solution by precipitation. Most of the time, it is calcium sulfate with two molecules of water dihydrate. The naming of the dihydrate process originates from this compound. If $CaSO_4 \cdot \frac{1}{2}H_2O$ is precipitated, it is a hemihydrate process.

A simplified reaction equation for the dihydrate process can be depicted as

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \longrightarrow 2H_3PO_4 + 3CaSO_4 \cdot 2H_2O \quad (1)$$

The reaction occurs in the presence of an excessively large amount of H_3PO_4. Equation (1) is an oversimplification of what actually takes place. The real occurrences within the reaction medium may be better described by subdividing Eq. (1) into three parallel and simultaneous reactions:

1. When sulfuric acid is dispersed in the reaction medium:

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-} \quad (2)$$

2. H^+ ions attack the phosphate rock particles which are introduced and dispersed in the slurry:

$$nH^+ + Ca_3(PO_4)_2 \longrightarrow 2H_3PO_4 + (n-6)H^+ + 3Ca^{2+} \quad (3)$$

The H^+ ions participating in this reaction "belong" to the sulfuric acid as well as to the excessive phosphoric acid in the slurry. There are about 25 times more H_3PO_4 than H_2SO_4 molecules.

3. Ca^{2-} ions encounter SO_4^{2-} with consequent crystallization:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O \quad (4)$$

These three reactions are well defined and have to be examined thoroughly one by one. All reactions take place in slurry reactors. When a degree of crystallization is achieved, the crystals are separated by filtration. In the case of a dihydrate process, phosphoric acid with a concentration of 25–31 wt % P_2O_5 will be obtained, according to the quality of the phosphate rock. With hemihydrate processes, this concentration can be substantially improved: 38–48% P_2O_5.

The separated crystals have to be washed thoroughly to yield at least 99% recovery of the filtered phosphoric acid. This is economically necessary because of today's raw material and energy costs. The primary objective during the reaction and crystallization operations is, respectively, to obtain a high yield of phosphoric acid from the phosphate ore and to maximize the recovery of P_2O_5 during filtration by optimizing the conditions that lead to the formation of easily filtrable crystals.

Looking at a dihydrate reaction system, we can distinguish two hypothetical stages as follows:

First stage: mixing and dispersion of the reagents within a large volume of slurry accompanied by a rapid reaction, complete within 85–95% of the total yield.

science

Second stage: the slurry from the first stage contains unattacked rock particles and gas bubbles and is supersaturated and hot. In the second stage, the reaction will be completed and the slurry will be deaerated, cooled, and desupersaturated to be recycled back to the first stage. The purpose of operating the reactions within a recycle loop is to keep mass and heat transfer rates within acceptable conditions for good crystallization.

2.2.1 First Stage: Introducing the Reagents

Sulfuric Acid

Sulfuric acid is generally fed into the reactor at a concentration of 98% and that means a concentration of 1793 g/liter. Within the reaction medium the sulfuric acid concentration is only between 10 and 40 g of H_2SO_4 per liter of 30% H_3PO_4.* Consequently, there has to be a very efficient dispersion of sulfuric acid in the slurry (about 1 volume to 90 in the case of a 20-g liter concentration). If this dispersion is not realized in good conditions, there will be spontaneous formation of crystal nuclei because of a state of what can be called "hypersaturation" due to SO_4^{2-} ions. Also, it is reported that poor sulfuric acid dispersion would generate anhydrite (SO_4Ca) formation. Anhydrite crystals are stable and disturb filtration.

By its dilution heat, sulfuric acid is responsible for most of the total heat of reaction. Overheated partial volumes of the slurry have to be avoided. Every contact between concentrated sulfuric acid and crystals results in immediate dehydration (opaque crystals are distinctly visible under the microscope). All this shows the necessity for vigorous and efficient dispersion of the sulfuric acid when it is fed into the slurry.

Fortunately, sulfuric acid helps itself in its intense dispersion. The violent generation of heat accompanied by vapor release creates intense turbulence where the sulfuric acid encounters the more dilute phosphoric acid. But this is not sufficient. Effective agitation (both flow and microdispersion) have to complete a perfect distribution of the H_2SO_4 within the reacting slurry volume. This is especially true for highly reactive rock, like that from Israel or Tunisia which needs more care in this respect than Florida rock, for example.

Another important factor has to be considered for both a high recovery of P_2O_5 from the rock and good crystallization; the sulfuric

*Sulfuric acid or SO_4 concentration mentioned in this book is always indicated as total acid or SO_4 as a result of gravimetric analysis. The acidimetric titration of H_2SO_4 in phosphoric acid does not indicate total SO_4; it is influenced by the impurities in the technical-grade acid. Sometimes, confusion results from the two methods.

acid has to be fed into a medium where a certain sulfuric acid concentration limit already exists. We shall see why in Section 2.2.3.

To ease the sulfuric acid dispersion, it is generally mixed first before being introduced into the slurry with recycle acid, a diluted phosphoric acid of about 16–19% P_2O_5 concentration, recycled from the filtration and cake wash sectors. The mixture of diluted H_3PO_4 and 98% H_2SO_4 reaches boiling point and releases some of the dilution heat in the form of vapor, which is evacuated from the reactor with other gaseous effluents.

For quite a long time it was believed that a preliminary dilution of the sulfuric acid from 98% to 80% with water would favor better crystallization. In fact, if the recycle acid/sulfuric acid mixture is properly operated, the H_3PO_4 concentration entering the reactor is exactly the same because of the total material balance. (The water added for sulfuric acid dilution has to be taken away from the filter cake wash water, and consequently the recycle acid is more concentrated.) The difference resulting from sulfuric acid dilution is noticed only in the heat balance; the heat removed by the sulfuric acid dilution-cooler does not have to be removed from the reactor. Furthermore, the practice of H_2SO_4 dilution, coupled with water balance constraints, reduces the availability of filter wash water. Consequently, higher P_2O_5 losses during filtration could be expected. The use of wet rock grinding and feeding has definitely killed the practice of sulfuric acid dilution; it would completely upset the filter wash water balance.

Phosphate Rock

Phosphate rock has also been subjected to sophisticated techniques for introduction into the reactor. Nowadays it is dumped in as it comes into a well-agitated slurry reaction tank, and it has never behaved as well. Prewetting with recycle acid as well as with recirculated slurry (for gradual attack) has been abandoned.

Phosphate rock particle size is another factor. This is a question of rock origin and also of process and equipment size. The rock fineness has to be sufficient to allow total recovery of the P_2O_5 by acid attack and avoid coating (see Section 2.2.3, "Introduction of the Phosphate Rock"). Large well-agitated tanks accept coarser rock for treatment. Some manufacturers just screen their rock through 0.5 or 1 mm and grind only the oversize; but, most of the time, particle size distribution is about 30–40% over 125 μm.

Some of the commercial phosphate rocks offer such size distribution as is, and no grinding is needed (Kola, Togo, Senegal, Bukraa, N. Carolina). With hemihydrate processes, coarser material can be processed because the reacting media is a low-sulfate phosphoric acid solution.

For the case of dihydrate processes, if phosphate rock is fed into a separate tank with recycled slurry, the sulfuric acid concentration

chosen. No particular comments on crystal habit modification by iron could be found in the literature. Fisons [97] states that needle and rhombic crystals were produced with rocks containing as much as 2% of F_2O_3, but those crystal shapes are common to many cases.

Magnesia. Most phosphate rocks contain about 0.2-0.6% of magnesia expressed as MgO. It is often said that Mg^{2+} impedes filtration of wet process acid either by affecting the crystal shape and size or by increasing the viscosity of the phosphoric acid. Besides the problems with filtration of the acid, the major concern for magnesium in phosphoric acid is, of course, the effect downstream on finished products, such as diammonium phosphate, where ammonium magnesium phosphate precipitates ($MgNH_4PO_4$). Analytical data of phosphoric acids show that all the magnesium is solubilized and stays with the 30% acid. No magnesium was found in the gypsum. Only after cooling in storage does $MgSiF_6 \cdot 6H_2O$ precipitate. Analytical data of phosphoric acids show that magnesium is solubilized and that most of it stays with the dihydrate product acid.

With hemihydrate conditions, that is, higher P_2O_5 acid concentrations, some of the magnesium can be found with the filter cake—obviously a compound with decreasing solubility in stronger acids ($MgNaF_6Al$?).

Since magnesia content is expected to increase in phosphate rocks to be mined in the future in central Florida, International Mineral Chemical Corporation has made pilot plant and industrial plant scale studies with phosphoric acid production from rock with a high MgO content, 1.5%, with a MgO/P_2O_5 ratio up to 0.053 [98]. During these test runs the overall efficiency of the P_2O_5 recovery dropped compared with other Florida rocks. The filtration rates were not said to deteriorate much; in fact, the filtration losses increased to about 0.5-1% of the total P_2O_5. Actually, this could be expressed as a decrease in filtrability of some 5% of the filter load to recover the previous yield. In spite of this, the filtrability remained above the figure of 7 tons of P_2O_5 per square meter per day at a filter speed of 4 min per revolution, and an acid concentration of 27-28% P_2O_5. The solids content of the slurry was 30 vol %, which is high and indicates crystals with a low surface-to-volume ratio. Cluster formation was observed under the microscope, (but this cannot be decisevely proven as resulting from the presence of magnesium, since cluster shape crystals very often form with Florida rock). No abnormal signs of scaling were observed and the magnesium silicofluoride $MgSiF_6 \cdot 6H_2O$ only precipitated from the 30% acid after cooling in storage. The viscosity of the acid increased in a way that indicates the strong effect of magnesium on this physical property.

Davister and Houghtaling [99] have also reported on phosphate rock containing high ratios of $MgO:P_2O_5$, more than 10%. Wet

process acid, they conclude, could be produced by accepting a weaker product acid, higher filtration temperatures, and thinner filtration cakes.

Calcium and Sulfate Ions. Calcium and sulfate ions come to an equilibrium governed by the solubility product (see Section 2.2.3) and it is not possible to consider the effect of these two separately. For reasons described previously, crystallization is generally operated in an excess SO_4^{2-} medium When Ca^{2+} ions are in excess instead of the SO_4 ions, only small, thin, losenge type crystals with poor filtration performances appear.

Fluorides and Silica. Fluorides and silica are present in all phosphate rocks. Fluorides, being associated with the apatite, generally occur with F/P_2O_5 ratios between 0.09 and 0.13 for sedimentary ores and can fall to 0.04 with igneous ores. For sedimentary ores the F/P_2O_5 ratio can be used as a reactivity indicator. Older deposits, those less reactive, generally show lower F/P_2O_5 ratios. Deposits such as those in Tunisia and North Carolina yield the upper level of reactivity and F/P_2O_5 ratio. High F/P_2O_5 ratios consequently can be used as an indicator for coating and enhanced cocrystallization tendency of the rock. The F/P_2O_5 ratio can also be used as the reactivity factor in computer programs for preliminary phosphate rock assessments.

Silica can be divided in two categories:

1. Reactive silica
2. Quarzite or unreactive silica

Reactive silica originates primarily from clays associated with gangue minerals intercalated with the phosphate ore. Hydrofluoric acid generated during the reaction is very silica-greedy, and if sufficient reactive silica is present in the ore, all the hydrofluoric acid will combine with it. The resulting H_2SiF_6 will, to a great extent, remain within the phosphoric acid solution or precipitate as fluosilcate (mostly sodium or potassium fluosilicate), depending on the amounts of Na and K available (see Section 3.5.2). Quarzite (sand) does not react quickly, and if not enough reactive silica is present, both HF in the liquid phase and SiO_2 as a solid in suspension will coexist in the slurry. In such a case, high corrosion rates must be expected (see Section 10.2.4). It has been demonstrated that the presence of fluorine entirely as H_2SiF_6 instead of HF or HF + H_2SiF_6 mixtures effects great changes in the crystal habit [96].

Rare Earth Compounds (Ce^{4+}, La^{3+}). Not much is known about the effect of rare earths on crystallization. Nevertheless, their

on crystal size. There is a second effect on crystallization due to the statistical retention time of the crystals in the different compartments of the reaction system. Crystals grow differently in the various sections of the reactor. Depending on reactor size, feed rate, and recirculation rate, the effective residence for crystals can vary widely, with dramatic effects on crystal sizes and size distribution. This is demonstrated in Section 2.3. (By "effective residence time" we understand to mean the residence time that crystals spend in a supersaturated reaction volume; a filter feed tank, for example, has no effective residence time.)

Hemihydrate and Dihydrate

Hemihydrate Formation. Calcium sulfate crystallization in phosphoric acid can have three different molecular compositions:

$CaSO_4 \cdot 2H_2O$	dihydrate
$CaSO_4 \cdot 0.5H_2O$	hemihydrate
$CaSO_4$	anhydrite

Whereas dihydrate is a well-defined crystal, hemihydrate is a solid solution. The water molecules are statistically inserted in the crystal pattern in poorly defined proportions. Usually, when produced in a wet process acid plant there is at least $0.5H_2O$, but it can vary in practice from 0.15 to 0.66 molecule of H_2O [103] according to the water concentration in the medium. Again, anhydrite is a well-defined crystal. From a phosphoric acid producer's standpoint, only dihydrate and hemihydrate are of importance; there is, at present, no plant working with anhydrite.

Dihydrate normally crystallizes when enough water molecules are available for its equilibrium and when the temperature of the crystallization media does not prohibit its formation. If the partial pressure of H_2O of the crystal becomes higher due to temperature, dihydrate crystals will dehydrate. Increasing H_3PO_4 concentration will reduce the partial pressure of the water molecules in the solution, and this will affect the temperature of the dehydration equilibrium.

Figure 2.40 depicts the thermodynamic equilibrium curves for dihydrate, hemihydrate, and anhydrate in phosphoric acid. This diagram has been discussed by a great number of authors and figures in many papers describing dihydrate and nondihydrate processes [104-109]. Curve 1 (Fig. 2.40) representing the dihydrate hemihydrate transition equilibrium, is the most important. All dihydrate processes work somewhere along that curve to produce the highest possible phosphoric acid concentration without hemihydrate formation.

But thermodynamic equilibrium is not the sole factor responsible for the different hydrate formations. To build a crystal there first

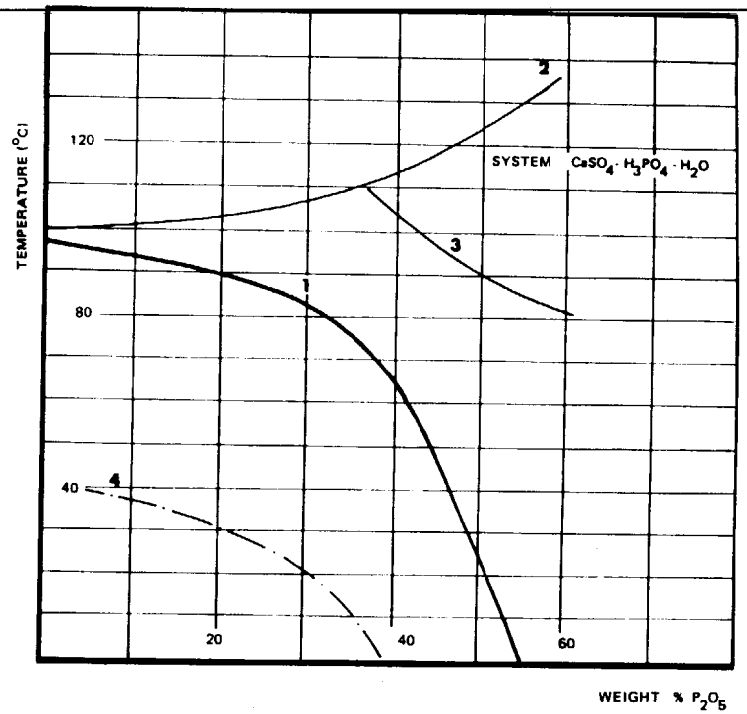

FIG. 2.40 System $CaSO_4/H_3PO_4/H_2O$. 1, Thermodynamic dihydrate-hemihydrate equilibrium curve. 2, Phosphoric acid boiling point. 3, Hemihydrate-anhydrite curve. 4, Metastable anhydrite curve. (From Ref. 1.)

has to be nucleation, and nucleation depends on solubilities and supersaturation. Now, each hydrate has its own solubility curve and each particular solubility curve is affected by phosphoric acid concentration and temperature. This, of course, complicates the system. Solubility and supersaturation limit lines affected by sulfate concentration and temperature are depicted in Fig. 2.41.

Consequently, if calcium sulfate is crystallized, its hydrate type will be that of its nucleation, the latter depending on the solubility diagram, even though precipitation occurs in the thermodynamically different zone. Dahlgren [111] and Vesteegh and Boontz [109] have explained these phenomena well in Slack's book. Table 2.4, resulting from Taperova's work [106,107], illustrates some dihydrate and hemihydrate solubility values according to temperature and concentration.

The reactivity of the phosphate rock is one of the variables promoting local supersaturation. This may explain why hemihydrate and dihydrate formation vary with the rock origin, although they may be precipitated in similar thermodynamical conditions. For example, dihydrate can be precipitated at higher temperature with Taïba rock than with Tunisian rock at the same acid concentration.

Sullivan and Kohler [112] published more data about calcium sulfate hemihydrate equilibrium in phosphoric acid (Fig. 2.42). Their investigation also covers the effect of impurities (Al, Fe, Mg, H_2SiF_6) on the equilibrium.

Hemihydrate-Dihydrate Recrystallization. When hemihydrate crystals are brought into a medium where temperature and phosphoric acid concentration equilibrate with the dihydrate phase (below curve 1 in Fig. 2.40), there will be recrystallization by means of dissolution:

$$3H_2O + 2CaSO_4 \cdot \tfrac{1}{2}H_2O \longrightarrow 2Ca^{2+} + 2SO_4^{2-} + 4H_2O \longrightarrow 2CaSO_4 \cdot 2H_2O \qquad (21)$$

At 60°C and 30% P_2O_5, for instance, the solubility of hemihydrate is well above that of dihydrate and the S line resulting from the presence of hemihydrate crystals provides enough supersaturation to ensure both dihydrate crystal growth and nucleation. Nevertheless, hemihydrate dissolution will never provide as high local supersaturation as that resulting from sulfuric acid or phosphate rock mixing with the slurry, and consequently nucleation of dihydrate seeds will be the factor limiting the speed of recrystallization.

Since recrystallization of hemihydrate to dihydrate operates via dissolution, all variables affecting the solubility of Ca^{2+} and SO_4^{2-} will also affect the recrystallization speed: temperature, phosphoric

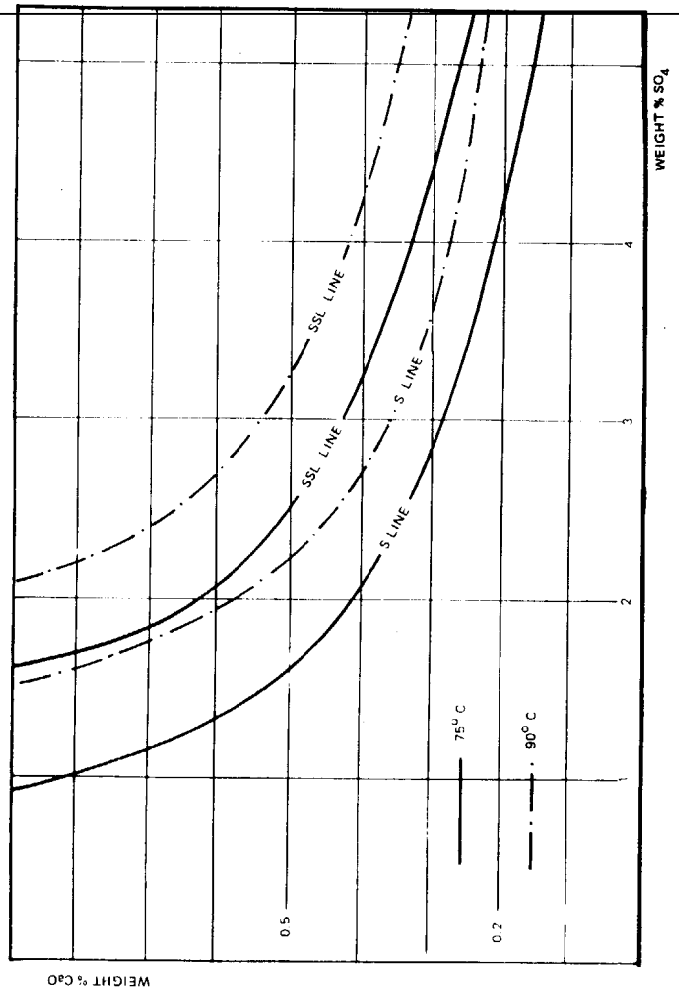

FIG. 2.41 Effect of sulfate concentration and temperature on calcium sulfate solubility and supersaturation limit lines in phosphoric acid slurries with 25% solid content in volume and 30% P_2O_5 in liquid phase. (From Ref. 110.)

for phosphate rock qualities that are sensitive to coating. For these cases the current rock fineness used should be around 25-40% over 0.125 mm, depending on rock quality, temperature, and process.

Critical sulfuric acid values have to be tested. Sometimes they are close to less than 1% of total SO_4^{2-}. Large reaction vessels are able to accept higher sulfuric acid excesses than are small vessels (lower feed ratio, less supersaturation).

Besides coated rock, bare unreacted rock P_2O_5 is rare. Unreacted rock is very difficult to determine with accuracy. The coated rock particles are by far the biggest particles in the slurry and therefore settle or separate very quickly. Depending on the sampling location, one can find very different values, sometimes changing by 100%. The recommended sampling location is from the filter feed slurry.

3.5 FLUORINE

Phosphate rock always contains fluorine. At F/P_2O_5 ratios, the fluorine content in rock of sedimentary origin ranges in general from 0.10 to 0.14. Rock of igneous origin shows lower ratios, from 0.04 to 0.06 (see Appendix A).

Calculating with fluorides or establishing the fluorine balance of a phosphoric acid plant is a very difficult matter, for the following reasons:

1. Analyses of fluorine and fluorides are tedious and often inaccurate.
2. Fluorides, once they have entered the reaction system, become volatile compounds, partially escaping the phosphoric acid slurry in various proportions.
3. Fluorides enter into many complex compounds, such as AlF_6^{3+} and SiF_6^{2-}.
4. Fluorides build many compounds with limited solubility in phosphoric acid, varying with temperature and phosphoric acid concentration, so that fluorides are permanently found in gas, liquid, and solid phases [2].

For example, if we want to know the fluorine content of the liquid phase in the reactor, we have to take a "live" sample from the reacting slurry by submerging a vacuum connected filtration funnel. A normal slurry sample carried to the laboratory for filtration would give an erratic picture.

3.5.1 Chemistry of Fluorine

When the phosphate rock reacts within the phosphoric acid slurry, hydrofluric acid is first produced:

$$(PO_4)_6Ca_{10}F_2 + 20H^+ \longrightarrow 6PO_4H_3 + 10Ca^{2+} + 2FH \qquad (87)$$

HF is a weak acid,

$$\frac{(H^+)(F^-)}{HF} = 10^{-3.2} \qquad (88)$$

But HF does not remain as such in the phosphoric acid slurry because of its strong tendency to react with silica.

With most phosphate rocks there is enough silica to allow a total hydrofluosilicic acid conversion:

$$6HF + SiO_2 \longrightarrow H_2SiF_6 \longrightarrow SiF_6^{2-} + 2H^+ \qquad (89)$$

H_2SiF_6 is a strong, totally dissociated acid.

To complete this reaction, silica has to be reactive silica, such as that contained in clays. If the silica content of the rock were only of the quartzite type, the reaction speed (because of the much lower surface area of the quartzite) would be too slow and hydrofluoric acid would remain in solution. In this case, HF will cause high corrosion rates on all the stainless steel parts of the equipment. Normally in such a case, the phosphoric acid producer adds reactive silica to complete the hydrofluosilicic reaction and to stop corrosion (see Section 10.2.4).

Because of the foregoing, the acid producer can thus assume that the fluorine in the acid is in practice present as H_2SiF_6. As a strong acid, H_2SiF_6 participates in the reaction with the rock, but SiF_6^{2-} ions also have a strong influence on crystallization of the gypsum, probably because of selective adsorption on crystal surfaces. The precise mechanism is not known and only experimental results can be reported on crystal shape changes related to H_2SiF_6 (see Section 2.2.5, "Effect of Impurities" and "Hemihydrate and Dihydrate").

The concentration of H_2SiF_6 in the reaction slurry is controlled by the alkaline cations Na^+ and K^+, both precipitating compounds with limited solubilities in phosphoric acid:

$$2Na^+ + SiF_6^{2-} \longrightarrow Na_2SiF_6 \quad \text{(sodium silicofluoride)} \qquad (90)$$

$$2K^+ + SiF_6^{2-} \longrightarrow K_2SiF_6 \quad \text{(potassium silicofluoride)} \qquad (91)$$

The solubilities of both compounds are shown in Fig. 3.8, but they vary from one author to another and probably with the rock origin and its impurities transferred into the acid.