

EXECUTIVE SUMMARY

1. GENERAL

Phosphoric acid is an important chemical used mainly as an intermediate by the fertiliser industry. A small proportion is used in soaps & detergents, metal treatment, food and beverage, etc. Pure phosphoric acid melts at 38.85°C, has a pleasantly sour taste when diluted and is weaker acid than Sulphuric or hydrochloric acids. Typical analysis of commercially available acid is given below in Table - 1.

TABLE - 1

TYPICAL ANALYSIS OF PHOSPHORIC ACID

Component	% by weight		
	Fertiliser Grade (Concentrated, H ₂ SO ₄ Acid Route)	Technical Grade (Concentrated, HCl Route)	Pure Grade
P ₂ O ₅	48	61	61
SO ₄	2.5	500ppm	--
F	2.0	30ppm	<20 ppm
Fe ₂ O ₃	0.30	20ppm	<20 ppm

2. MANUFACTURING PROCESS

Phosphoric acid is produced either by acidulation of phosphate rock by a mineral acid in a wet process or by burning of phosphorus produced through electro-thermal process.

Processes using sulphuric acid are the commonest and most important and may be classified according to the hydrate form in which calcium sulphate crystallises, viz, anhydrate (CaSO₄), hemihydrate (CaSO₄.1/2H₂O) and dihydrate (CaSO₄.2H₂O). The hydrate form is controlled mainly by temperature and acid concentration. Table-2 gives the salient,

TABLE-2

**SALIENT FEATURES OF CONTEMPRARY PROCESS TECHNOLOGIES FOR FERTILIZER GRADE
PHOSPHORIC ACID (SULPHURIC ACID ROUTES)**

S. NO.	Name of the Process	No. of Sepa	Data Furnished by Process Licensors							Gypsum Quality
			ration Steps	Capital cost (1988) for 600 TPD P ₂ O ₅ Plant. Million \$ (Rs. (Crores)	P ₂ O ₅ recovery (%)	Filtrate Concentra tion% P ₂ O ₅	Temperature °C	Energy Require- ment per ton P ₂ O ₅	L.P. Steam. Ton	
1.	Dihydrate	1	29	95.0-96.0	26-32	70-85	--	125	2.5	Not good
2.	Hemihydrate- Dihydrate									
	(a) Conventional	1	29 (43)	98.0	26-30	70-- 100	50-60	110	0.2	Good
	b) MODIFIED	2	31 (46)	98.0-98.5	40-50	90-- 100	50-65	--	--	Excellent
3.	Dihydrate	2	31 (46)	98.0-99.0	35-38	65-70.	90-- 100	110	--	Excellent
4.	Hemihydrate	1	25 (37)	93.0-94.0	40-50	80 100	--	100	0.2	Reported Poor

features of contemporary process technologies (using sulphuric acid) in commercial use. The features listed include P_2O_5 recovery efficiencies, filtrate concentration (% P_2O_5), specific energy consumptions (electricity and low pressure steam), temperature conditions required to be maintained in reactor and recrystalliser and quality of by-product gypsum. Approximate investment in phosphoric acid plants varies from Rs.2,100/- to Rs.2,600/- per annual tonne of P_2O_5 .

The conventional dihydrate process remains the most predominant because of its low capital cost, low operating temperatures and flexibility of operation. But, inspite of the various modifications, each striving to produce rapidly filtrable gypsum crystals, lower P_2O_5 losses and produce acid of higher concentration, the dihydrate process suffers from relatively low P_2O_5 recovery and low strength of acid.

Newer process which claim to overcome these limitations of the dihydrate processes are hemihydrate-dihydrate (double filtration stage) and dihydrate-hemihydrate.

Hydrochloric acidulation process produces technical grade acid. After acidulation, the acid has to be concentrated and purified before use in detergent or food industry. Capital cost and cost of production are higher than those for sulphuric acidulation plants though the cost differential is reducing gradually with improvements in the HCL process.

Electro-thermal reduction of phosphate rock produces very pure phosphoric acid, but the cost of production is extremely high because of high cost of power in India. Capital cost is the highest for plant based on this technology.

The present status of all these processes have been discussed in detail in Chapters-V and VI.

3. RAW MATERIALS

The major raw materials, viz, phosphate rock and sulphur are both imported. Limited quantity of phosphate rock available in the country is of low grade and none of the phosphoric acid plants utilises it because of its poor grindability and reactivity properties. Production of phosphoric acid in India is thus based totally on imported phosphate rock.

4. ENVIRONMENTAL PROBLEMS

Waste gases containing fluorides and large quantities of waste slurry containing phosphogypsum are the two pollution problems in phosphoric acid plants. Efficient scrubbing of gases

with water removes fluorides thus minimising air pollution. The recent trend is towards recovering gypsum in the dry state and use it for manufacture of gypsum board, cement, etc. though even now large quantities of gypsum are dumped in open space.

5. CORROSION AND MATERIALS OF CONSTRUCTION

Phosphoric acid is corrosive to most materials of construction. Because of the presence of impurities in rock phosphate, the problems of corrosion and erosion are very complex. The common materials of construction in wet acid plants are listed in Table-3.

TABLE-3

COMMON MATERIALS OF CONSTRUCTION FOR PHOSPHORIC ACID

Service	Materials of Construction-
Phosphate rock handling	Concrete, carbon steel.
Digestors, Scrubbers	Rubber-lined steel, concrete with brick lining.
Reactors, filters, pumps, agitators	316L, 317L, Alloy-20, CD-4MCu, HV-9
Heat exchangers	Graphite

6. INTERNATIONAL SCENE

6.1 Global Phosphoric Acid Capacity

Last two and a half decades have seen a tremendous build-up of wet phosphoric acid capacity in the world. While the early 1960s saw expansion in phosphoric acid capacity in North America, Western Europe and Japan, major expansions during the late 1960s and the 1970s took place in North Africa, South Africa, the Middle East, Eastern Europe and USSR, particularly near phosphate rock mines. During a span of 24 years, the share capacities of Western Europe and North America have

reduced to nearly half, while those of Eastern Europe and Africa have increased nine and four times, respectively. The present wet phosphoric acid annual world capacity is about 38 million tonnes of P_2O_5 while production is about 25.7 million tonnes of P_2O_5 .

Conventional dihydrate process continues to be the most used process. Even among new investments, dihydrate systems will dominate because of safe technology required for many new projects with new rocks in remote places. Nevertheless advanced technology involving hemihydrate formation will also progress, essentially in plants with high CIF phosphate rock costs and particular energy problems.

6.2. Trends in Technology Development

Current development work in phosphoric acid technology is concentrated towards the following:

- Reduction in consumption of energy.
- Decreasing quality of phosphate rock.
- Protection of environment.

Examples of recent improvements in phosphoric acid plants are:

- Use of open-circuit wet grinding of rock to increase plant throughput.
- Purification schemes for wet process phosphoric acid for removal of impurities originally present in low-grade rock.
- Effluent treatment through closed circuit loops for total containment of effluents within the system.

7. STRUCTURE OF PHOSPHORIC ACID INDUSTRY IN INDIA

FACT Udogmandal set up in 1960 the first commercial wet phosphoric acid plant with an installed capacity of 8000 TPA of P_2O_5 . The two decades thereafter saw a significant growth in the manufacture of phosphoric acid with installed capacity

increasing to 2.00 lakh TPA of P_2O_5 by 1970 and further to 6.60 lakh TPA of P_2O_5 by the end of 1980.

Over the years, the size of plants also registered an increase, going upto 1.00 lakh TPA of P_2O_5 . Paradeep Phosphates' plant, which is under construction, has rated capacity of 2.25 lakh TPA of P_2O_5 .

There are presently thirteen (13) wet phosphoric acid units in the country, out of which twelve are based on sulphuric acid route and one on hydrochloric acid route. Two of the plants are closed because of problems of equipment breakdown. Out of the three(3) thermal phosphoric acid units in the country, two have discontinued production because of high electrical power requirement resulting in very high production cost.

With the commissioning of Paradeep Phosphates and Hindustan Fertiliser Corporation's plants, the total installed capacity will increase to about 9.151 lakh TPA of P_2O_5 by the year 1989-90.

The estimated demand of fertiliser grade phosphoric acid in the country in 1989-89 is 15.1 lakh tonnes while projected demand for the year 1994-95 is 24.9 lakh tonnes P_2O_5 . The corresponding figures for technical and foodgrade phosphoric acid are 38,600 tonnes P_2O_5 and 58,000 tonnes P_2O_5 respectively.

Imports of phosphoric acid during last few years have registered a very sharp increase due to the setting up of a number of di-ammonium phosphate plants, with indigenous phosphoric acid capacity remaining more or less stagnant. Even with the existing capacity, capacity utilisation, in general, of phosphoric acid industry in India is below 60% (except for 2-3 units achieving more than 85% capacity utilisation). This utilisation factor is very low in comparison with international standard.

Major problems affecting productivity are: mechanical breakdown of equipment; shortage of power, other extraneous factors like limitations in availability of raw materials, water, storage space for product acid, etc. Common mechanical breakdown problems are: failure of rubber lining in various equipment and pipe lines; failure of rubber lined diaphragm valves, exhaust fan, slurry pumps, filter rollers, etc. Varying characteristics, namely, grindability, reactivity, filterability and impurities,

of phosphate rocks from different origins also affect productivity.

8. TECHNOLOGICAL STATUS OF INDIAN INDUSTRY

All the phosphoric acid plants in India are based on foreign technology. Nine phosphoric acid units (including one under construction) are based on conventional dihydrate process, which accounts for 65% of the wet phosphoric acid installed capacity based on sulphuric acid. Three plants (including one under construction) are based on hemihydrate-dihydrate process (accounting for 12% of the installed capacity) and two plants are based on dihydrate-hemihydrate process (accounting for 20% of the installed capacity). The last mentioned plants are not in operation because of problems of equipment breakdowns.

Considerable operating experience has been gained in operating plants based on conventional dihydrate process which for nearly three decades now, has been the most tried and established process in the country. Performance of these plants has been generally satisfactory with units like Coromandel Fertilisers Limited and GSFC Limited, consistently achieving high levels of capacity utilisation and good P_2O_5 recoveries.

Plants based on hemihydrate-dihydrate process have also performed reasonably well, with SPIC Limited reporting about 98% P_2O_5 recovery. There are no phosphoric acid plants in India based on hemihydrate or modified hemihydrate-dihydrate process.

Collaborations in case of dihydrate processes have been with Prayon and Dorr Oliver/Jacobs International Inc. (3 Nos. each) and Chemico and Sim-Chem (1 no. each). Nissan has supplied technology for hemidihydrate plants through its licensees, PDIL for two plants and Hitachi Zosen for one plant. For di-hemihydrate plants, FEDO was the licensee for Central Glass-Prayon's process. IMI has supplied the hydrochloric acid-solvent extraction process for Ballarpur Industries' plant through AEA, France. The three thermal acid plants employed TVA's know-how.

The earliest plants were implemented by foreign, as well as, Indian engineering contractors, namely, FEDO, PDIL, Hindustan Dorr-Oliver Limited, DMCC Limited and Krebs & Cie Limited.

Table -- 4 lists the process followed, the installed capacity, process licensor & engg. contractor for each of the phosphoric acid units in the country.

TABLE--4

TECHNOLOGICAL STATUS OF INDIAN INDUSTRY

(CAPACITY IN TONNES P₂O₅)

S.No.	Manufacture	Installed Capacity	Process Licensor	Engineering Contractor
A. PLANTS BASED ON CONVENTIONAL DIHYDRATE PROCESS				
1.	FACT Limited Udyogmandal	33,000	Dorr Oliver, U.S.A.	Hindustan Dorr Oliver, Ltd.
2.	EID Parry, India Limited	10,696	Societe-de-Prayon, Belgium	Simon Carves Ltd. U.K.
3.	GSFC Limited	52,500	Chemico, USA through Hitachi Zosen, Japan	Hitachi Zosen, Japan
4.	Coromandel Fertilisers Ltd.	91,000	Dorr Oliver, USA	Dorr Oliver USA
5.	Albright Morarji & Pandit Ltd.	17,385	Societe-de-Prayon Belgium through Albright & Wilson, UK	Dharamsi Morarji Chemical Co. Ltd.
6.	FACT Limited, Cochin	1,18,800	Societe-de-Prayon Belgium through FEDO	FEDO
7.	Hindustan Zinc	26,000	Not available	Not available
8.	Hindustan Lever Limited	41,850	Mechim/Simchem	FEDO
9.	Paradeep Phosphates Ltd. (under construction)	2,25,000	Jaçobs International Inc. with Indian associate Hindustan Dorr Oliver Ltd.	Hindustan Dorr Oliver Limited

S.No.	Manufacture	Installed Capacity	Process Licensor	Engineering Contractor
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B. PLANT BASED ON HEMIHYDRATE-DIHYDRATE (NISSAN PROCESS)

1.	RCF Ltd.	30,000	Nissan, Japan	PDIL
2.	SPIC Ltd.	52,800	Nissan, Japan	Hitachi Zosen Japan
3.	HFC LTD. (under construction.)	27,600	Nissan, Japan through PDIL	PDIL

C. PLANTS BASED ON DIHYDRATE-HEMIHYDRATE (CENTRAL GLASS-PRAYON PROCESS)

* 1.	Hindustan Copper Limited	68,000	Societe-de-Prayon, Belgium	FEDO
* 2.	FCI Limited	1,19,000	Societe-de-Prayon, Belgium	FEDO

D. PLANTS BASED ON HYDROCHLORIC ACID PROCESS

1.	Ballarpur Industries Ltd.	24,000	AEA France (IMI Process)	Krebs & Cie Pvt. Ltd.
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E. PLANTS BASED ON THERMAL PROCESS

1.	Star Chemicals (Bombay) Pvt. Ltd.	6,000	TVA, USA
*2.	Excel Industries Limited	N A	TVA, USA
*3.	Transpek Industry Limited	N A	TVA, USA

* Plants not in operation

9. R&D ACTIVITIES

Except for some research work at CGCRI on utilisation of by-product gypsum, no specific work for development or improvement of phosphoric acid and related

technology has been done at the National Laboratories. Some of the phosphoric acid manufacturers have reported some R&D work on improvement/modification in the processes imported. Some have modified effluent disposal systems and have also developed methods for better utilisation of gypsum.

FEDO, PDIL, GSFC Ltd., Albright Morarji & Pandit Ltd., Coromandel Fertilisers Ltd., SPIC Ltd., and Ballarpur Industries Ltd., are the companies who have reported doing some R&D work pertaining to phosphoric acid. Unfortunately, there has been very little commercial application of the inhouse R&D work done in the country.

10. TECHNOLOGY ABSORPTION AND MODERNISATION EFFORTS

For the earlier phosphoric acid plants, the cost of imported equipment used to vary between 70% to 90% of the total plant and machinery cost. With gradual indigenisation, equipment import cost has come down to around 25% for example, in the case of the currently under-construction plant of Paradeep Phosphates Limited. Most of the equipment like reactor, vessel, cooler, scrubber, grinding mill, conveyor, thickener, submersible pumps, etc. are now indigenously available, but critical equipment and components like digester, agitator, filter, special pumps, carbate heat exchanger, carbon bricks, etc., are still imported. This is because either the special materials of construction like 317L, Alloy- 20, HV-9 CD-4MCu, carbate, good quality rubber and cement, etc., required for their fabrication are not available in the country or sometimes because of lack of confidence of the licensor/owner in indigenous equipment manufacturers' capabilities, imports result. A few of the reputed Indian manufacturers of pumps, heat exchangers, etc. have recently entered into technical collaboration with internationally known companies for manufacturing some of the equipment still being imported.

Though the Indian phosphoric acid industry has been in existence for more than 25 years and many of the manufacturers have the technical competence required for technology absorption, it is unfortunate that very little research and 'know-why' exercises necessary for understanding the chemistry and design parameters of the imported process have been reported by the companies. Concrete efforts for modernisation have also been rare, with the result that many of the phosphoric acid plants are saddled with old equipment which have frequent breakdowns.

11. RECOMMENDATIONS

Based on the study, the following major recommendations can be made.

- Build-up of adequate indigenous capacity to avoid ever-increasing imports of phosphoric acid.
- Improvement in the productivity of existing plants by ensuring adequate availability of power, replacing worn-out equipment, installing more efficient reactors and filters (at some of the plants), purchasing phosphate rock of similar composition and following systematic preventive maintenance programme.
- A major development programme for acidulation with nitric acid should be taken up in view of danger of limited availability of sulphur in world market. Efforts for better utilisation of indigenous pyrites and the sulphide ores of zinc, copper and lead should be made.
- Extensive geological survey to locate new reserves for phosphate rock and installation of beneficiation plants for low grade rock of M.P. and U.P. may be considered for the Eighth Plan period.
- Dihydrate process incorporating new improvements or the two stage hemidi-hydrate process should be considered for new plants in India. There is no need to import technology again for projects for the improved dihydrate process.
- Indigenisation of capital equipment should be facilitated by making special materials available at a reasonably low import duty and also allowing Indian equipment manufacturers to obtain designs from reputed suppliers abroad.
- National laboratories and phosphoric acid manufacturers should direct their R&D efforts towards developing indigenous technology using indigenous beneficiated rock, improved hydrochloric acidulation and nitric acidulation processes, process using mixture of sulphuric and nitric acids, economic methods for purifying wet phosphoric acid and newer and more efficient uses for by-product gypsum and fluorine compounds. The goal should be to commercially apply the promising results achieved.