INCEPTION OF THE WORLD'S LARGEST PHOSPHORIC ACID PLANT

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Introduction

In early 1996, Oswal Chemicals and Fertilizers Limited initiated activities to set up a phosphate fertilizer project to produce about 3 MM tons/year of granular fertilizers at Paradeep in Orissa State, India. Initial questionnaires to prospective technology suppliers were requested in July 1996. Proposals for the component plants were received in February 1997 with contract award in April 1997. The plant is due on stream April 1999.

At the time of writing, basic engineering is complete, detailed engineering is approximately 30% complete, the long lead major equipment items have been purchased (reactor agitators, ball mills, five belt filters, the reactor and evaporator axial flow pumps, gypsum slurry pumps, and evaporator heat exchangers) and construction of the foundations is underway.

The capacity of the phosphoric acid plant is 2650 metric tons per day of phosphoric acid in a single line. The plant is designed for Florida, Senegal, Jordan, Moroccan, and Togo phosphates.

Description of Plant

MER .1   65 BPL

The overall layout of the plant is shown in Diagram (1). Rock is fed from storage to two 550 ton unground rock storage silos. (A) via a weigh feeder to two parallel 1200 kW wet ball mills operating in closed circuit; (B) Ground rock underflow from the screen system is collected in the slurry surge tank; (C) Each rock grinding system is designed for 65% of the plant flowsheet capacity. Two grinding trains were selected to enhance plant availability and to move the capacity of the ball mills within the proven range of indigenous suppliers.

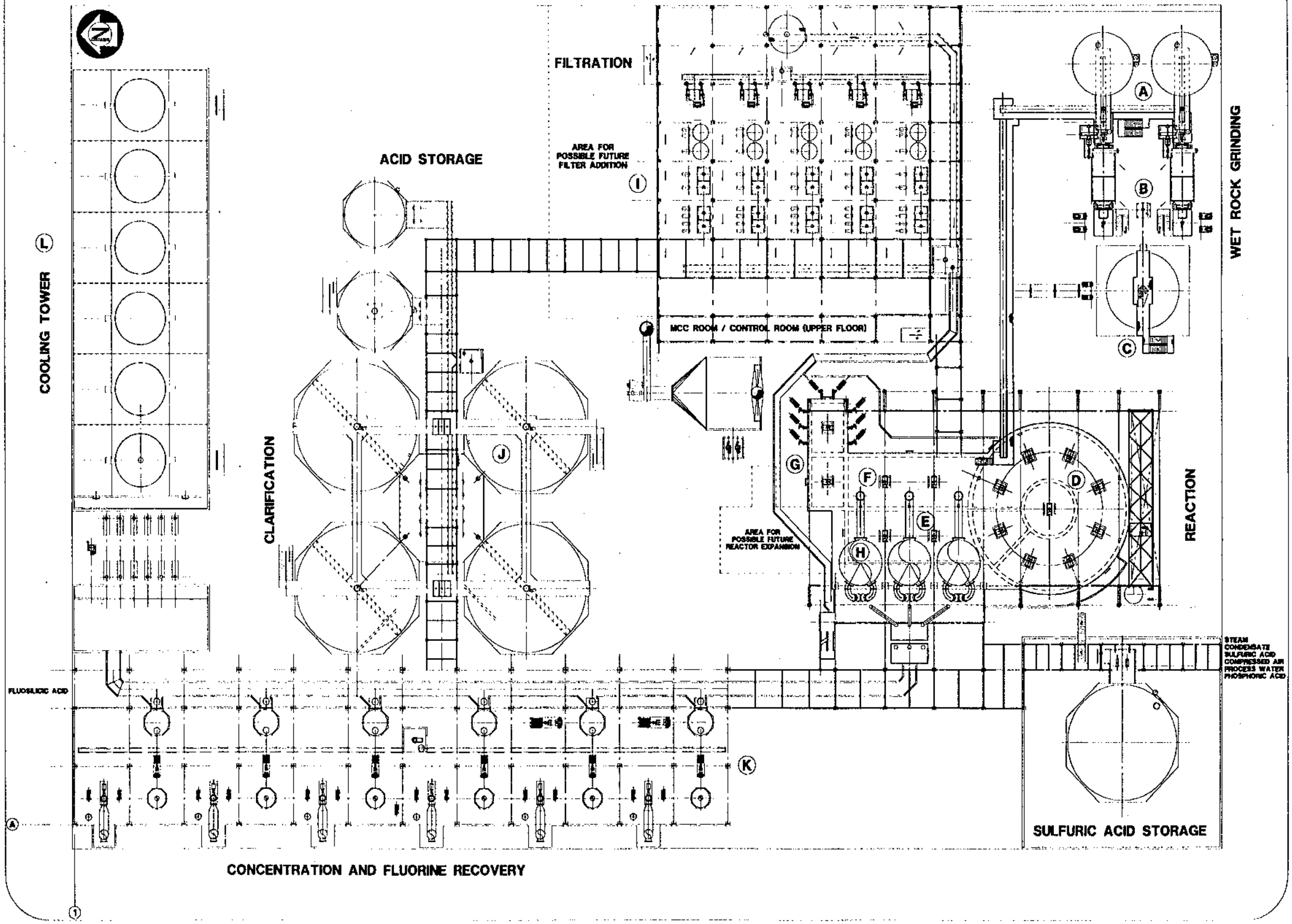
The phosphate rock is fed to Jacobs' annular phosphoric acid reactor (D). The total reaction volume provided is 4240 m^3, 2300 m^3 in the annular reactor, 770 m^3 in each of the cooler feed and cooler seal tanks (E) and (F), and 400 m^3 in the adjustment and filter feed tank (G). The annular reactor at 25 meters diameter is a 25% extension from Jacobs' current largest operating unit.

$\frac{2650 \text{ metric Tons}}{4240 \text{ m}^3}$

Three low level 7.1 m diameter vacuum coolers (H) are provided, these are similar in diameter to the Jacobs' existing installation at Paradeep. Each is fed with a 9000 m^3/hr. axial flow pump. Similar pumps of this capacity are in operation at the Rotem plant in Israel. This vacuum cooler circulation provides a low 2.7°C temperature drop across the vacuum cooler minimizing vacuum cooler downleg scaling. Back-mixing around the annular section of the reactor adds about 13,500 m^3/hr. to the circulating flow. High sheer, 220 kW agitators are provided in the rock addition section of the reactor with high flow 150/185 kW agitators elsewhere. The agitators supplier has supplied individual reactor agitators up to 1000 kW in phosphoric acid reactor service elsewhere.

The slurry from the reactor system is fed to four operating and one spare 110 m^2 belt filters (I). These units are similar to those operating at the Namhae plant in Korea. The filters incorporate four washes. Byproduct gypsum is sluiced with pond water and pumped to a gypsum stack for disposal.

DIAGRAM 1
OSWAL 2650 MTPD PHOSPHORIC ACID PLANT



Product phosphoric acid is pumped to one of two 4,000 m^3 (J) evaporator feed tanks and then to five operating and one spare single staged forced circulation, evaporation and fluorine recovery units (K). These units are identical to units installed on the Jacobs' phosphoric acid plants in Hubei Province in China. Each evaporator station includes a 6.4 m diameter calandria 7300 m^3/hr. recirculation pump and 760 m^2 impervious graphite tube heat exchanger. The evaporation system is designed for a 2.5°C temperature rise on the phosphoric acid side to minimize scaling and to extend time between cleaning. The evaporator overhead passes through a 5 m diameter entrainment separator to remove entrained phosphoric acid then to a fluorine scrubber system which produces 18% fluosilicic acid. Evaporated acid is stored in two 4,000 m^3 clarification tanks.

Heat is removed from the reaction system in the reactor vacuum cooler condensers and from barometric condensers in the evaporation section. The hot cooling water flows via trenches to the hot well of the cooling towers and is pumped from the hot wells to one of six cooling tower cells (L).

The unit is designed for 95% plant availability whereas 85% is more common for phosphoric acid installations. The provision of two 65% rock grinding systems, three vacuum coolers, and spare filtration and evaporation units will allow the plant to operate through conventional descaling and maintenance activities.

Choice of Reactor

Hemihydrate technologies were excluded because the largest hemihydrate reactor in operation has a capacity of 1100 MTPD. The four dihydrate processes available basically divide into two types. Two of the processes - Raytheon [Figure (1)] and Rhone-Poulenc [Figure (2)] - are large single tank systems with a centrally mounted agitator and a high recirculation rate.

2 650 metric Ton
1000 man power

Figure (1) Raytheon Reactor System

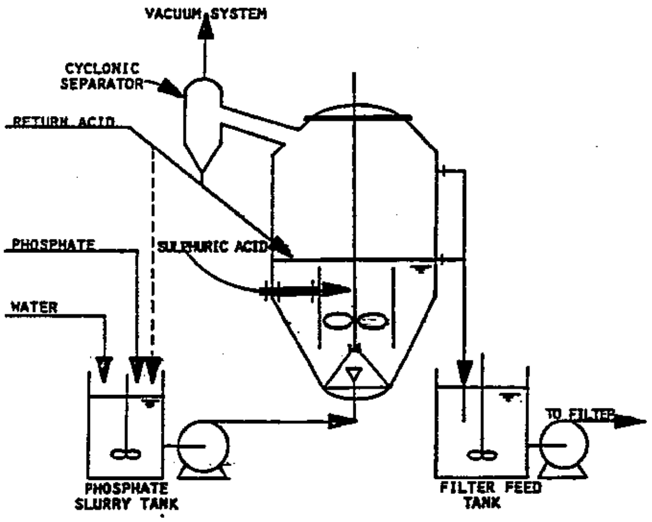
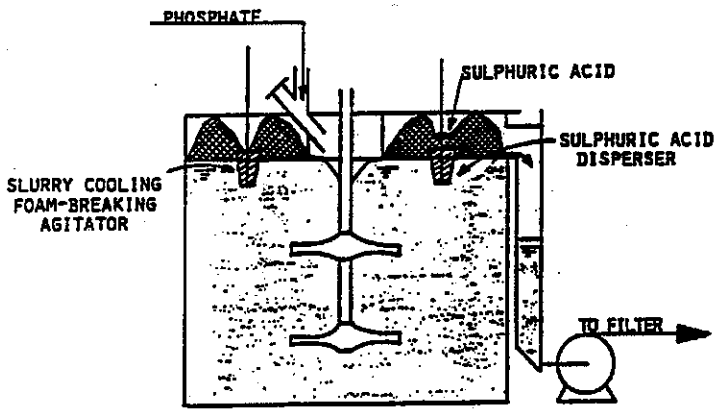


Figure (2) Rhone Poulenc Reactor System



The other two processes - Prayon [Figure (3)] and Jacobs [Figure (4)] incorporate a progressive flow of recirculating slurry through a long reactor path with the addition points for phosphate rock and sulfuric acid separated.

Figure (3) Prayon Reactor System

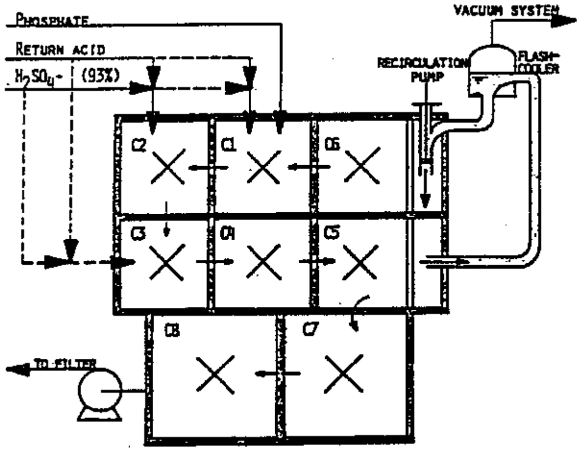
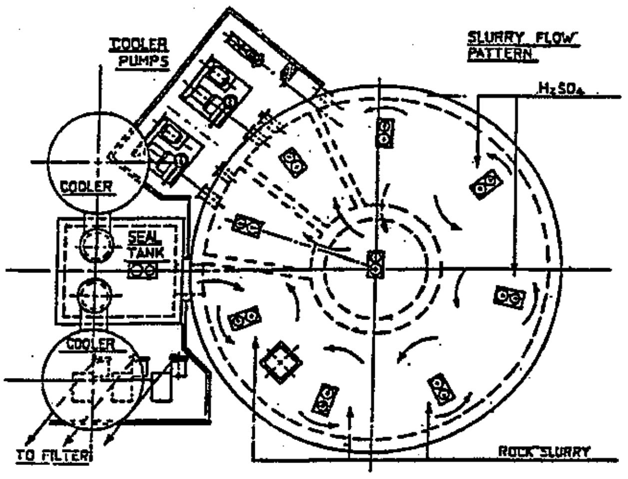
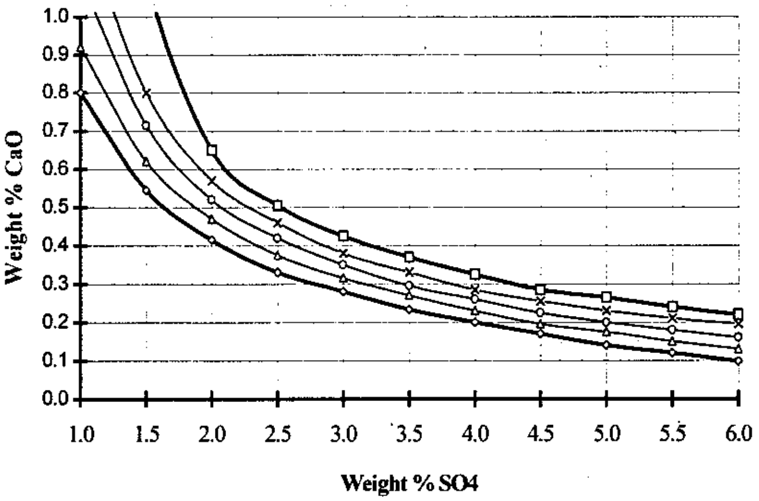


Figure (4) Jacobs Reactor System



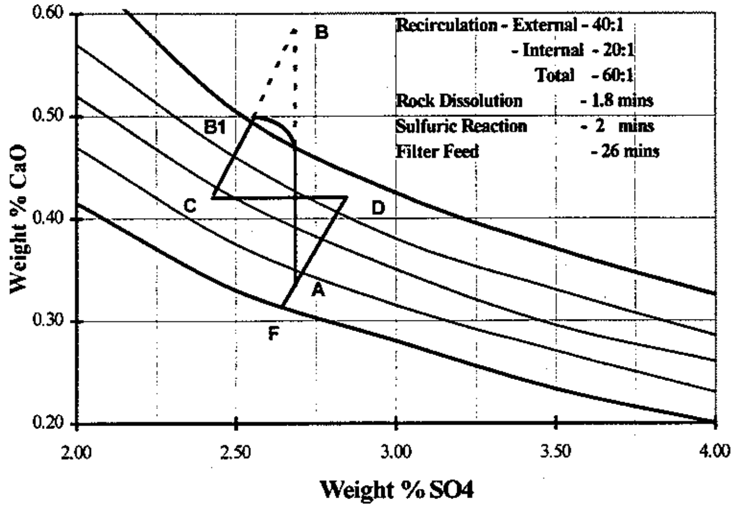
The main difference between the two types of processes can be appreciated by plotting the course of the dissolution of phosphate rock, gypsum crystallization, and sulfuric acid addition on the gypsum crystallization diagram,(1) Figure (5). This crystallization diagram plots fixed gypsum crystallization rates against percent weight concentrations of free Ca and SO_4 ions in 30% P_2O_5 wet process phosphoric acid. The bottom bold curve is the saturation line. Below this line no crystallization occurs. The upper bold curve is the supersaturation line. Above this line, spontaneous nucleation occurs with the formation of millions of very small crystals or "nuclei". If phosphoric acid reactors are operated too far into this region, the system produces very small gypsum crystals which are difficult to filter.

Figure (5) - CaSO4 Crystallisation



Between the two bounding curves crystallization is mainly by the growth of existing crystals. The faint curves represent lines of constant crystal growth rate. The optimum operating point for a phosphoric acid reactor is mainly between the saturation and supersaturation lines. Figure (6) follows the progress of rock dissolution and gypsum formation in a Jacobs phosphoric acid reactor.

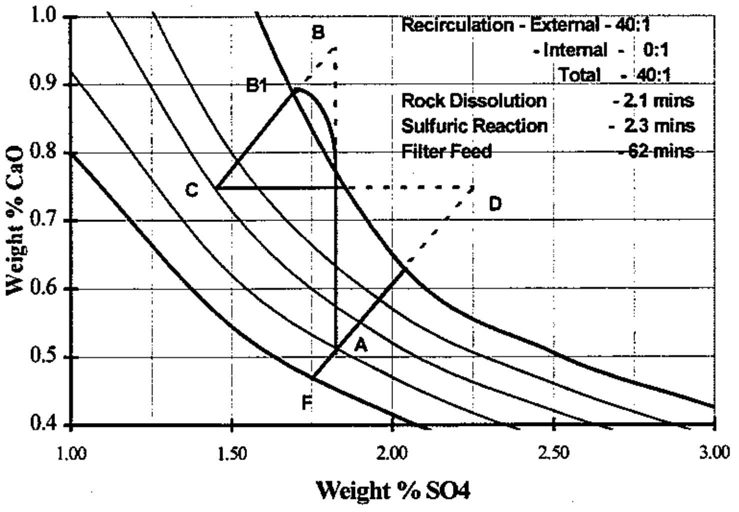
Figure (6) - Jacobs Crystallisation



Jacobs phosphoric acid reactors typically operate with an external slurry recirculation ratio (circulating slurry to filter feed) of 40:1. Dye tests in Jacobs reaction systems have shown that the induced recirculation in the annulus of the Jacobs reactor is approximately 20:1. Slurry returning from the vacuum cooler seal tank to the first agitator at (A) with a 2.65% w/w SO_4 concentration feeds to the first agitator as does the phosphate rock feed slurry. If the phosphate rock were to dissolve instantaneously and if no gypsum crystal growth would take place, the conditions in the reactor would go to point B. However, Becker has shown(1) that it takes a couple of minutes to dissolve the majority of the phosphate rock and this is indeed the residence time in the phosphoric rock dissolution zone. In addition, the gypsum formation reaction competes for Ca ions so it is likely that the concentrations in the phosphate rock dissolution area follow the locus A to B1 to C. Sulfuric acid diluted with return acid from the filter is added at agitator four and is almost instantaneously dispersed into the slurry in this area. Sulfuric acid addition will therefore follow the line C to D and the remaining gypsum formation, the line D to A. It should be noted that point A is not on the saturation curve as some gypsum formation driving force is required throughout the reactor system. The filter feed is matured in the filter feed tank for 20-30 minutes to remove any traces of gypsum supersaturation and reduce scaling tendencies due to the formation of sodium or potassium aluminum fluosilicate (line A to F).

Figure (7) shows a similar phosphate rock dissolution/gypsum formation profile for a true compartmented process like the modern Prayon process.

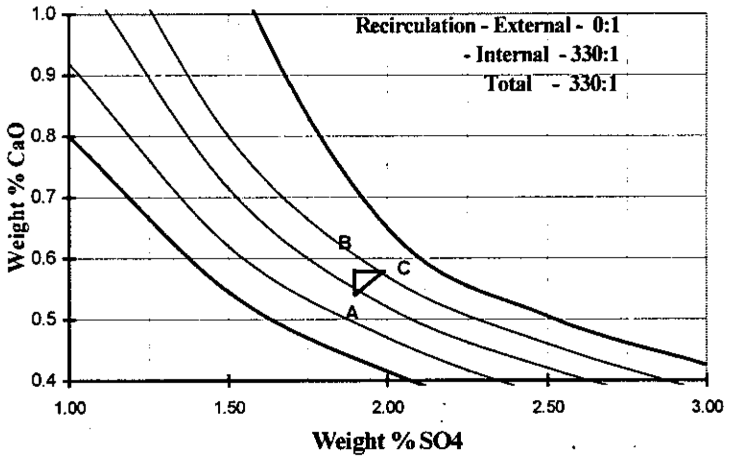
Figure (7) - Prayon Crystallisation



The major differences between this unit and the Jacobs process are; no internal recirculation; an overall recirculation ratio of about 40:1; more of the reactor devoted to filter feed retention (about an hour) and the need to operate at lower sulfate concentrations in the rock dissolution area because of rock particle occlusion and sulfate instability (see below). The reactor works at lower sulfate concentrations and higher Ca ion concentrations in the rock feed compartment, moving the whole reactor away from the optimum, more horizontal part of the gypsum crystallization curve to the more vertical part. As a result of this and the lower recirculation ratio, sulfuric acid addition pushes the system into the nucleation zone.

Figure (8) shows the rock dissolution reaction diagram for a single tank reactor system.(2)

Fig. (8) - Raytheon Crystallisation



Here the centrally mounted agitator induces a recirculation ratio of 330:1 and as a result, the phosphate rock and sulfuric acid are distributed very quickly throughout the reactor system resulting in very small changes in concentration and a homogenous system. The advantage of this system is that spontaneous nucleation is avoided except perhaps at the point of sulfuric acid addition. However, this same high recirculation ratio prevents the contents of the reactor from achieving the high sulfate concentrations and crystal growth rates seen in either the Prayon or Jacobs reactor after sulfuric acid is added.

Becker(1) in work on hemihydrate recrystallization to gypsum saw a correlation between increasing sulfate levels and the size of the gypsum crystals produced and drew a parallel between that and gypsum crystallization from the phosphoric acid gypsum sulfuric acid slurry. With a given phosphate rock, the single stirred tank system would, therefore, be expected to produce smaller, less filterable gypsum.

One area where all three reaction systems are working on similar phosphate rocks in plants with similar operating skills and an incentive to produce at maximum rate is central Florida. Table (1) is a comparison of Jacobs, Prayon and Raytheon reaction/filtration systems in the central Florida area. All of the systems are distinguished by the significant improvement over nameplate achieved by their operators. The Jacobs and Prayon designs achieve similar Reactor and Filter productivities, as would be expected from the similarities of the two processes. However, the filtration rate of gypsum from this single stirred tank reaction system is only half that of the progressive flow reaction systems. We believe that similar results would be achieved by the Rhone-Poulenc reaction system which has the added disadvantage of high fluorine emissions or an expensive fluorine scrubbing system because of the use of air cooling.

All of the filters on the plants listed in Table (1) were of the table or tilting pan type operating at similar filter cycle times and the results are therefore comparable. Clearly the most economic plant would be found in one of the progressive flow reactors, either Jacobs or Prayon.

Table (1)
Relative Reaction and Filtration Rates

	Technology	Reactor Productivity Design $t/m^3/d$	Filter Productivity Design $t/m^2/d$	Reactor Productivity Achieved $t/m^3/d$	Filter Productivity Achieved $t/m^2/d$	Achieved Capacity over Nameplate
	metric Tons					
Cargill	Jacobs	0.49	4.8	1.2	12	2.44
	Prayon (Old)	0.83	7.8	1.3	12	1.57
	Prayon (New)	0.80	8.6	1.1	11	1.38
	Raytheon	0.64	3.5	1.1	6	1.72

Reactor Stability

Figure (9) was presented at the AIChE meeting in Clearwater discussing problems with sulfate control on a new Prayon reactor configuration.

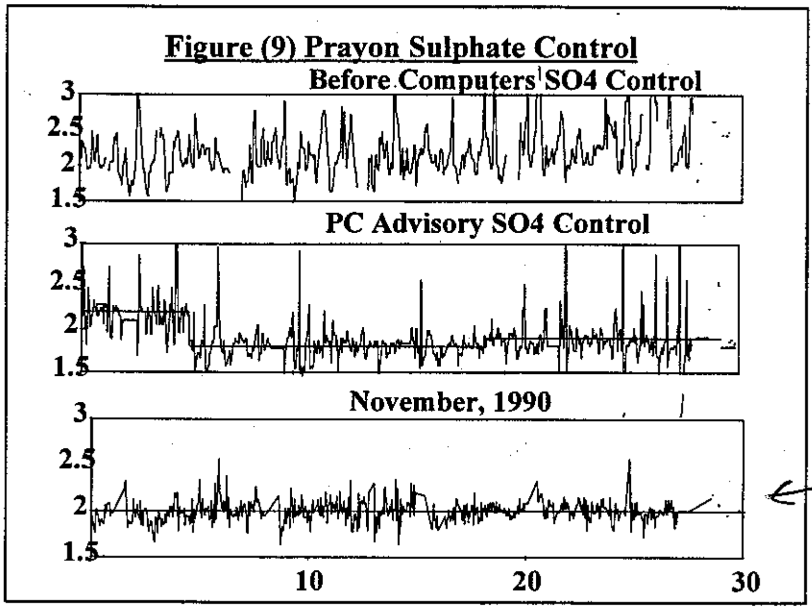


Figure (9) Prayon Sulphate Control

computer control

The unit was operating at a production rate of about 1 t $P_2O_5/m^3/d$ on central Florida phosphate. The instability shown "before supervisory control" is caused by occlusion of the rock particles by small gypsum crystals which leads to slower rock dissolution rates and progressively higher sulfate concentrations. The operator then reduces the sulfuric acid feed rate to the reaction system inducing low sulfate readings then increases the sulfuric acid feed rate, and so on. The mean SO_4 ion levels are about 1.8%.

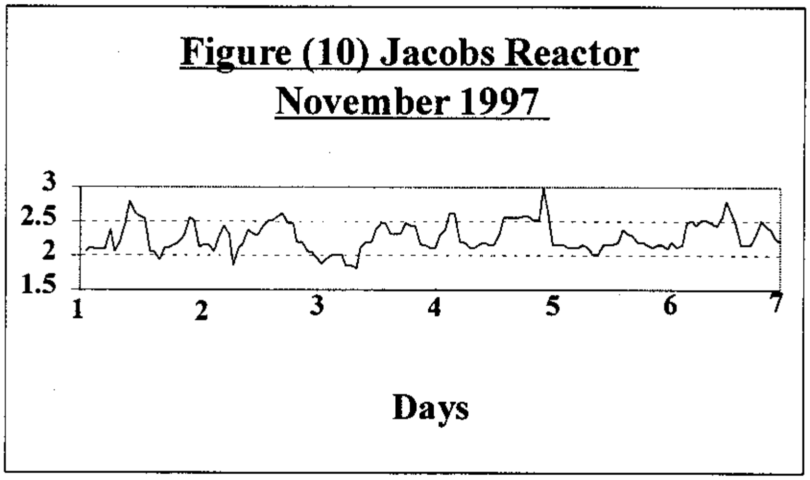


Figure (10) Jacobs Reactor November 1997

Figure (10) shows a Jacobs reactor system operated at the same reactor productivity of 1.1 t $P_2O_5/m^3/d$. on a similar phosphate rock.

Daily sulfate swings are about half that seen in the other reactor system. Simple flow control is used for the reactants. The operator of the Prayon system developed first a reactor operation advisory program and then direct on line sulfate control to improve the stability of their reaction system.

The difference between the two reaction systems is that sulfuric acid and phosphate rock are added to the open annulus of the Jacobs reaction system whereas in the Prayon reactor they are added to discrete compartments. Instantaneous flow changes in the rock and sulfuric acid caused by control "hunting" and variability in rock dissolution characteristics are equilibrated throughout the large annulus of the Jacobs reaction system and are less likely on an instantaneous basis to drive the local sulfate ion concentrations in the reactor system to the level that rock occlusion and sulfate excursions occur. Another possible reason for the apparent difference is that more of the reactor volume is assigned to the reaction loop in the Jacobs system and less to filter feed storage.

The induced recirculation in the Jacobs reactor makes it especially suitable for treating low grade rocks, unreactive rocks and rocks containing high concentrations of iron, aluminum and magnesium.

The Jacobs reactor was favored for the Oswal project on the basis of minimum size and cost at a given capacity for both reaction and filtration areas and ease of operation and stability.

Choice of Filter

Three types of filter have been conventionally used for separation of gypsum from phosphoric acid:

1. The rotary tilting pan filter as manufactured by Bird Machinery Co., and Profile, SA Belgium
2. The horizontal table filter sold by Aoustin known as the Ucego filter, and
3. Traveling belt filters available from several different suppliers (Eimco, Delkor, Filtres Philippe, etc.)

A study was conducted by Jacobs in 1990 comparing a 162 m^2 Bird 30D filter, a 153 m^2 Ucego 11, and two 65 m^2 belt filters. The required belt filtration area is lower because of a faster cycle time. Table (2) compares the capital and three year operating costs of the filter stations.

Table (2)
Filter Station Cost Comparison

Filter station, Type	Total Installed Cost	3 yr. operating cost
Eimco (2 x 65 m^2)	100	100
Ucego No. 11 (153 m^2)	125	108
Bird-Prayon 30 D (162 m^2)	125	109

The operating cost includes maintenance power, evaporator steam to compensate for dilution and operating supplies. It can be seen that belt filter costs are lower. In addition, plants with multiple belt filter installations do not need to shut down the reaction/evaporation systems during maintenance. As Jacobs has no preference on filter type and will provide its phosphoric acid plant with whatever the client prefers a belt filter system was selected.

Proprietary Items

Jacobs required no proprietary equipment to be used with its technology. Other technology suppliers required the purchase of a proprietary filter and proprietary agitators. It was thought that the use of proprietary equipment would add substantially to the cost of the phosphoric acid plant.

Project Execution

Jacobs is a large engineering company with revenues of $1.8 billion, a total engineering staff of 10,000, and three engineering offices in India with a staff of approximately 1,000. They were able to offer process technology, basic engineering, detailed engineering, and construction management from a single source with a significant Indian presence. Other technologies would have required the teaming of three much smaller entities to provide the licensing, basic engineering, detailed engineering and construction aspects of the project. Having all of the required resources in one company seemed to be an advantage.

Conclusion

In 1991 Jacobs presented a Paper at the AIChE conference in Clearwater, Florida entitled "Phosphoric Acid Technology for the Nineties". In that paper we predicted a next level of production with a reaction system of 2,600 m^3 of slurry volume, larger than any system then and now in operation. The Oswal project far exceeds that vision.

References

1)Pierre Becker, Phosphates and Phosphoric Acid, Second Edition, Marcel Dekker, New York, 1989, Chap 1

2)John L. Martinez and W. Douglas Belle, Phosphorus & Potassium, 211, p47 (Sept/Oct 1997)

2-2.5% +35

Cargill Reactor recirculation

20:1 $\frac{\text{Cargill}}{\text{Internal}}$

40:1 external