PHOSPHORIC ACID TECHNOLOGY FOR THE NINETIES

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INTRODUCTION

Phosphoric acid is a mature technology. It has been around since the 1920's and before. Changes have come slowly. January 1991 marked the 60th anniversary of the beginning of the modern dihydrate process. In 1931, the Dorr Company managed a workable dihydrate process out of an unsuccessful hemihydrate design at the Trail, B.C. plant of Cominco. Prior to 1931, the technology was similar to that shown in Figure 1, which was the Anaconda Montana countercurrent decantation plant typical of the 1920's. Such processes made 22% P_2O_5 acid, or thereabouts.

The Dorr flowsheet is shown in Figure 2. It was a cascade digestion system with substantial circulation of gypsum slurry and liquid phase sulfate control in the range we still use today. This plant made about 120 TPD P_2O_5 in 3 lines at a filter acid strength of 31% to 32% P_2O_5; it achieved good, filterable gypsum and stable operating conditions.

Similar cascade-recirculated phosphoric acid plants were built through the 1950's .

By that time, St. Gobain, the predecessor of present day Rhone Poulenc, had introduced their single tank process. In 1959, the smelter at Bunker Hill, near Kellogg, Idaho, needed a phosphoric acid plant to consume smelter sulfuric acid. They rather fancied the St. Gobain process.

Bill Weber, one of the developers of the 1931 Dorr "Strong Acid Process", came up with Dorr Oliver's annular "Single Tank" reactor as a result of direct pressure by the Bunker Hill management. It was rather a compromise design, somewhere between the Dorr or Prayon cascade systems and the true single stirred vessel of St. Gobain. His original patent is shown in Figures 3 and 4 showing an air cooled unit.

Dorr-Oliver went on in the 1960's to build over twenty of the annular reactors. The flow pattern of Dorr's first vacuum cooled system at Agrico South Pierce is shown in Figure 5. Table 1 shows operating results from the test run at that plant. At 360 short tons per day P_2O_5, the reactor had 8 hours detention. This relatively large reactor, plus high slurry recirculation inherent in the annular reactor, a large filter size (620 sq. ft. active) for the capacity, and a relatively fine grind, gave the highest recoveries in Florida at that time (1966), 96.9% in gypsum repulp slurry samples at an average No. 1 filtrate strength of 31.2% P_2O_5.

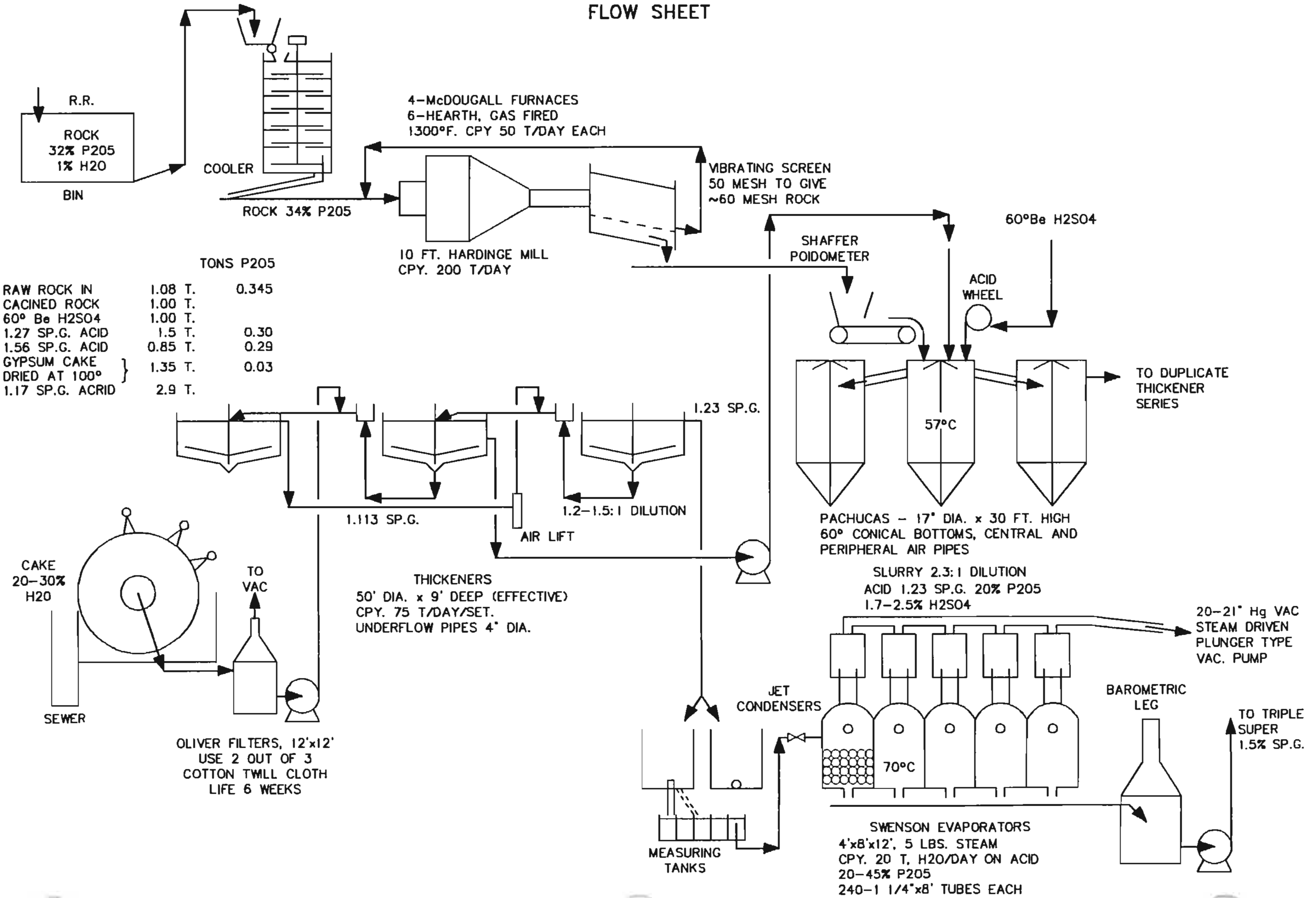
During the 1970's, as plants in Florida pushed for increased output, operation at high rates uncovered flaws or bottlenecks in the plants then in operation. For the Dorr plants, a shift to vacuum cooling set up a path of short circuiting and flow patterns had to be modified. In general, operators sought higher slurry recirculation rates to reduce insoluble losses, up-flow vacuum coolers were disappearing and wet rock without sulfuric acid dilution cooling was entering the scene. This revamp period which started in the 1970's is still going on and is likely to be most of the activity in Florida during the 90's.

JE

ANACONDA PLANT

ACID SECTION

FLOW SHEET



		TONS P205
RAW ROCK IN	1.08 T.	0.345
CACINED ROCK	1.00 T.	
60° Be H2SO4	1.00 T.	
1.27 SP.G. ACID	1.5 T.	0.30
1.56 SP.G. ACID	0.85 T.	0.29
GYPSUM CAKE DRIED AT 100°	1.35 T.	0.03
1.17 SP.G. ACRID	2.9 T.	

FIG[illegible]E 1

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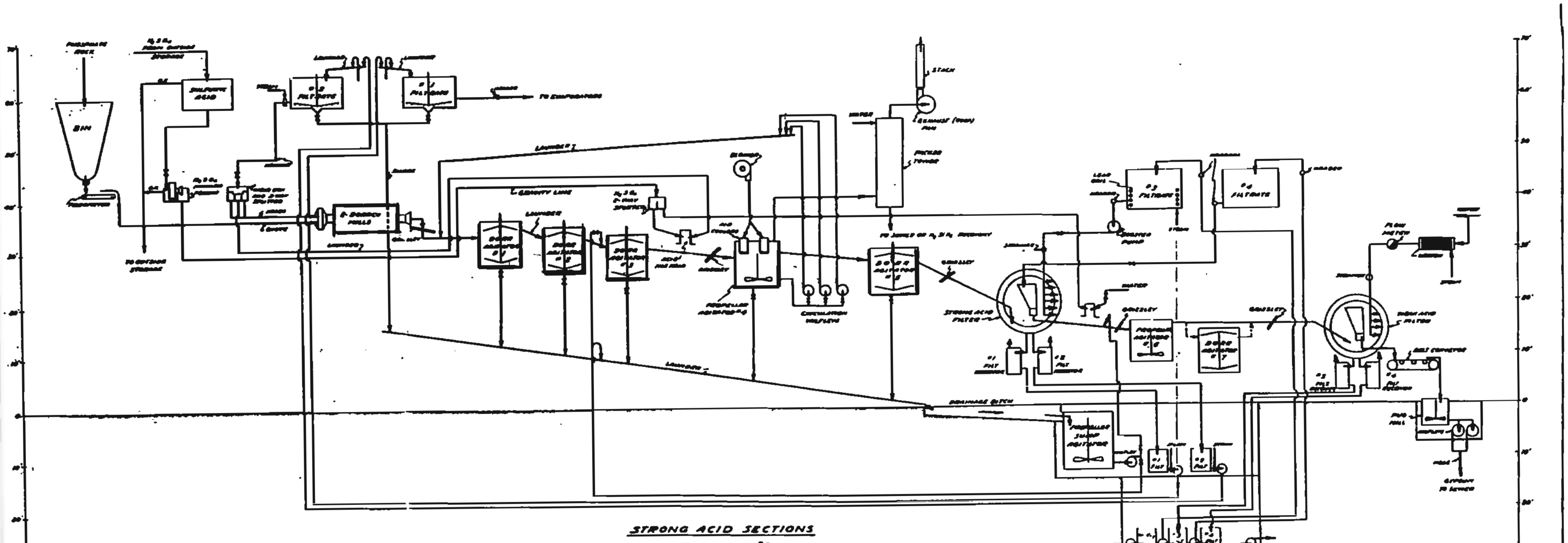


DORR DIHYDRATE PHOSPHORIC ACID PROCESS

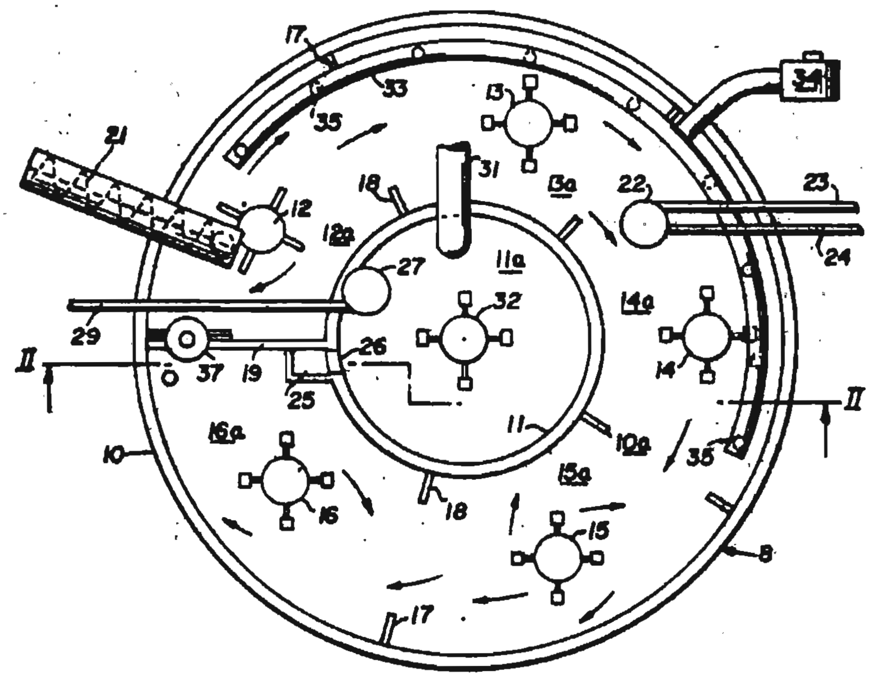
AT TRAIL

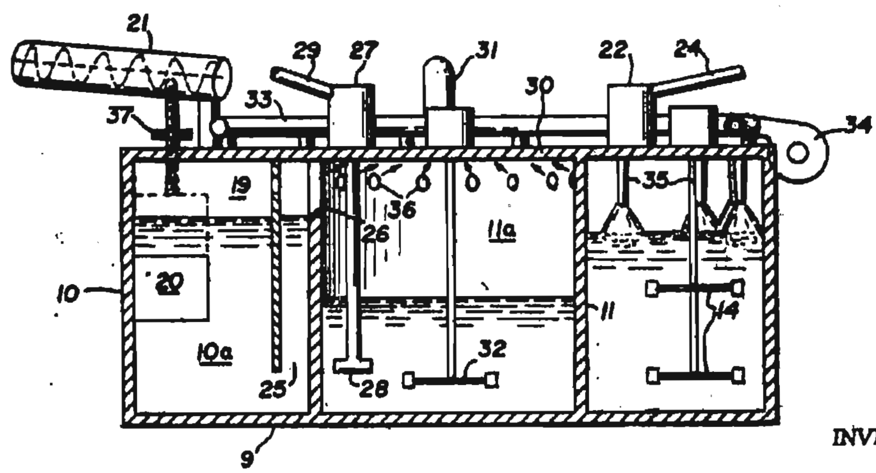
Figure 2

May 4, 1965 W. C. WEBER 3,181,931

PROCESS FOR PRODUCING PHOSPHORIC ACID

Filed Feb. 19, 1962 2 Sheets-Sheet 1





INVENTOR

WILLIAM C. WEBER

Figure 3

May 4, 1965 W. C. WEBER 3,181,931

PROCESS FOR PRODUCING PHOSPHORIC ACID

Filed Feb. 19, 1962 2 Sheets-Sheet 2

FIG. 3

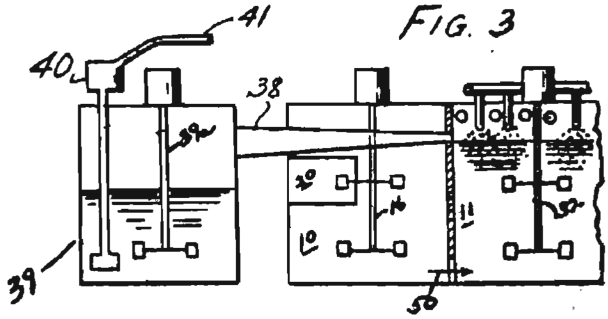


FIG. 4

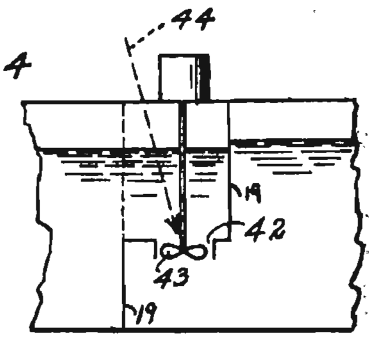
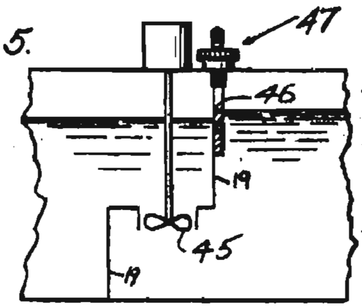


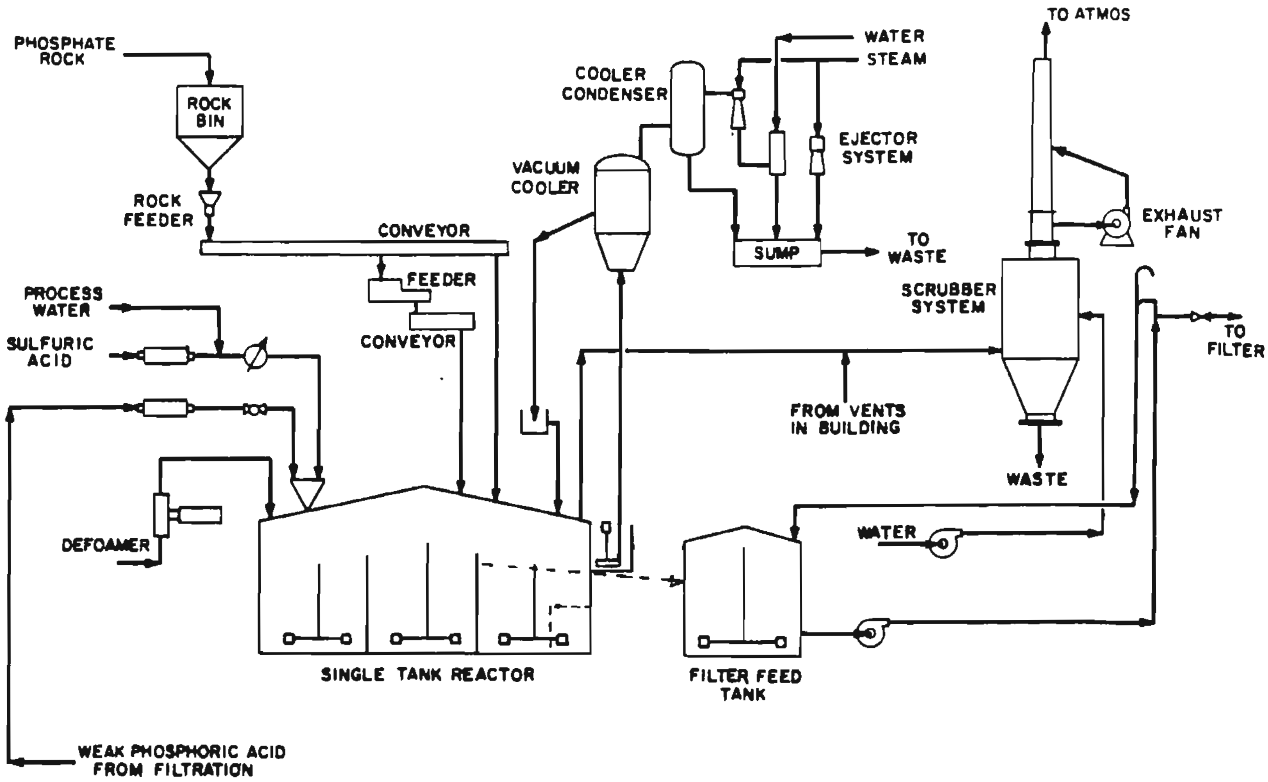
FIG. 5.



INVENTOR.

WILLIAM C. WEBER

Figure 4



Dorr-Oliver reaction system (vacuum-cooled)

Figure 5

Table 1

Operating Results, B-Train, A.A.C.

Date Shift		Tons P_2O_5 Fed	Losses, % of P_2O_5 FED Insol.	Water Sol.	Misc.	Recovery D & F	Tons P_2O_5 Prod.
9/19	1		2.14	2.15	0.06	95.7	
	2	342	2.14	1.38	0.05	96.4	329
	3		2.00	0.50	0.08	97.4	
9/20	1		3.63	0.70	0.05	95.6	
	2	379	2.21	0.87	0.05	96.9	365
	3		2.40	1.05	0.06	96.5	
9/21	1		2.02	0.45	0.01	97.5	
	2	382	2.02	0.74	0.01	97.2	371
	3		2.07	1.25	0.01	96.7	
9/22	1		2.40	0.41	0.05	97.1	
	2	365	1.97	0.49	0.04	97.5	355
	3		2.26	0.64	0.04	97.1	
9/23	1		2.24	0.83	0.15	96.8	
	2	393	2.05	0.53	0.14	97.3	382
	3		2.00	0.46	0.13	97.4	
Ave.		372	2.24	0.83	0.05	96.9	360

RECENT PLANTS BY JACOBS

In 1982, Gardinier put on line the first phosphoric acid plant done by Jacobs with the technology they had acquired from Dorr-Oliver. The annular reactor, shown in Figure 6, incorporated modifications demonstrated in the Dorr plants at Agrico, CFI and Occidental.

The configuration shown in Figure 6, which Jacobs calls it's "high throughput mode" is relatively spartan. There is only an attack zone, no post-treatment zone and no filter feed tank. Considering the small size of the reactor, only 1500 m^3 (53,000 cu. ft.), relatively high throughputs are achieved, well above 1.0 T P_2O_5/m^3 of slurry volume.

At the other end of the spectrum is the Cominco arrangement shown in Figure 7. This concrete reactor started operation in 1985. It replaced an earlier Dorr reactor which was installed with a low level, flooded vacuum cooler in 1970. The new Cominco configuration has what we term an adjustment compartment where rock for desulfation can be added, or where sulfuric acid can be added to reduce supersaturation, or where simply, some aging can take place.

Jacobs' phosphoric plants for the Hubei projects in China, to come onstream in the mid nineteen nineties, will have this configuration, except for the addition of supplemental recirculation as shown in Figure 8. Here, part of the recirculation bypasses the cooler, specifically to reduce the temperature of the filter feed by 3°C to 4°C. This configuration is judged to be the most flexible to deal with the high impurity Chinese rocks on which there is little commercial plant experience.

In the arrangements shown here, with post treatment, Jacobs devotes from 15% to 22% of the total reaction volume to the "adjustment" and filter feed services. This is more than provided in some of the true single tank processes but also less than one well-known process vendor who devotes as much as one-third of the total volume to the post-treatment function. We believe it is difficult to justify such a large volume because it inherently subtracts from the attack volume. In the Jacobs' reactor, where a relatively large percentage of the volume of the reactor is maintained in the open annular part, a

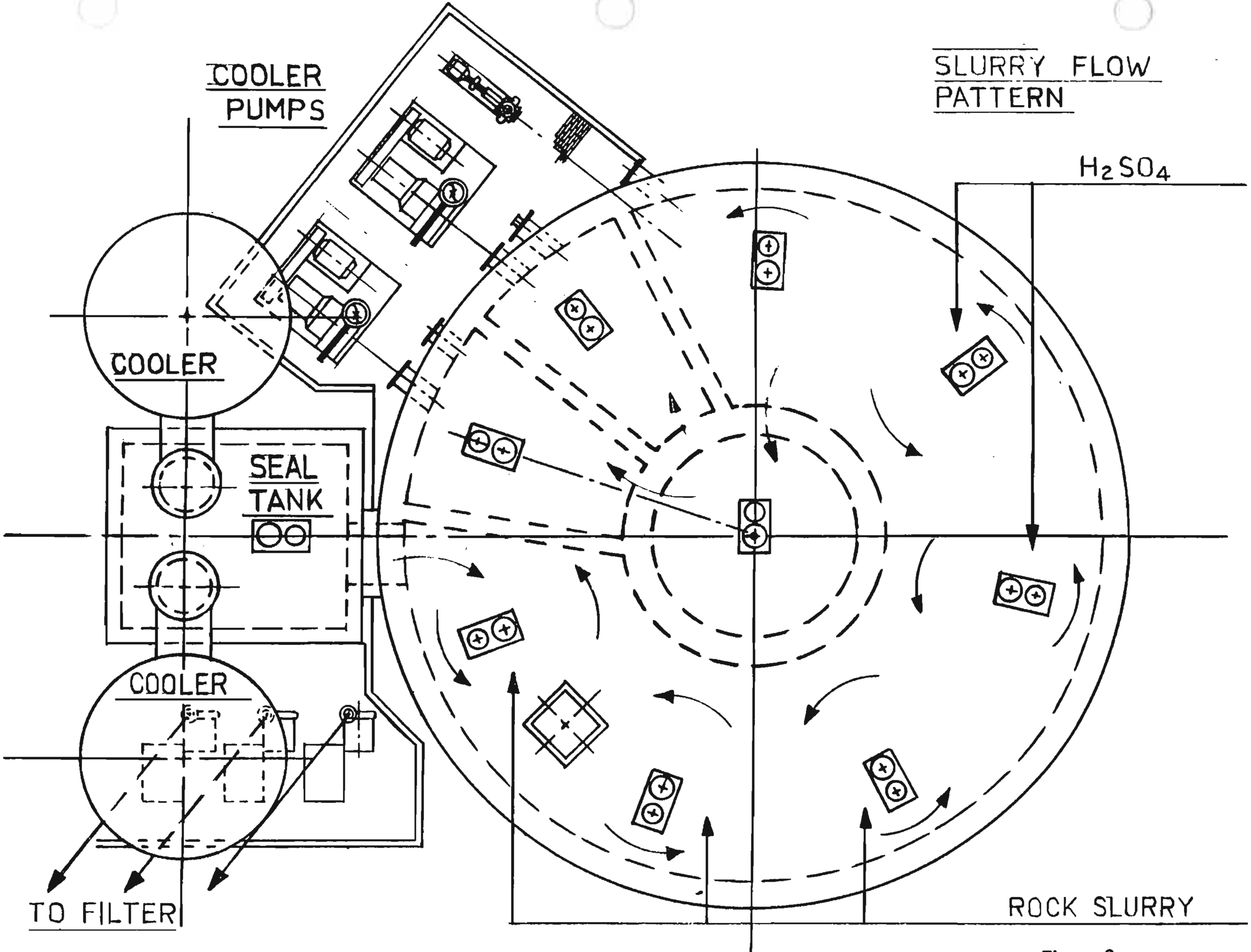

COOLER
PUMPS
SLURRY FLOW
PATTERN
H_2SO_4
COOLER
SEAL
TANK
COOLER
TO FILTER
ROCK SLURRY

Figure 6

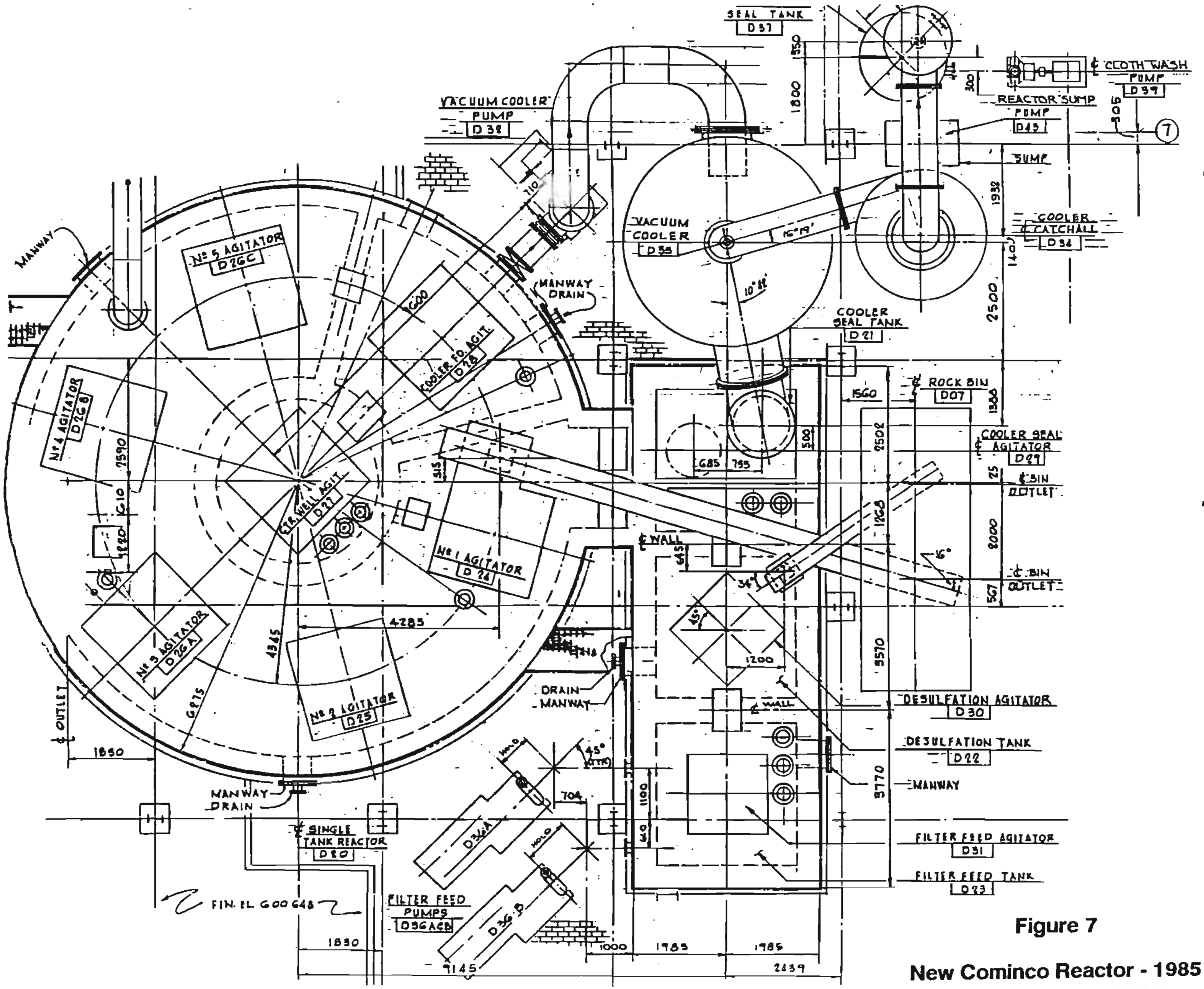
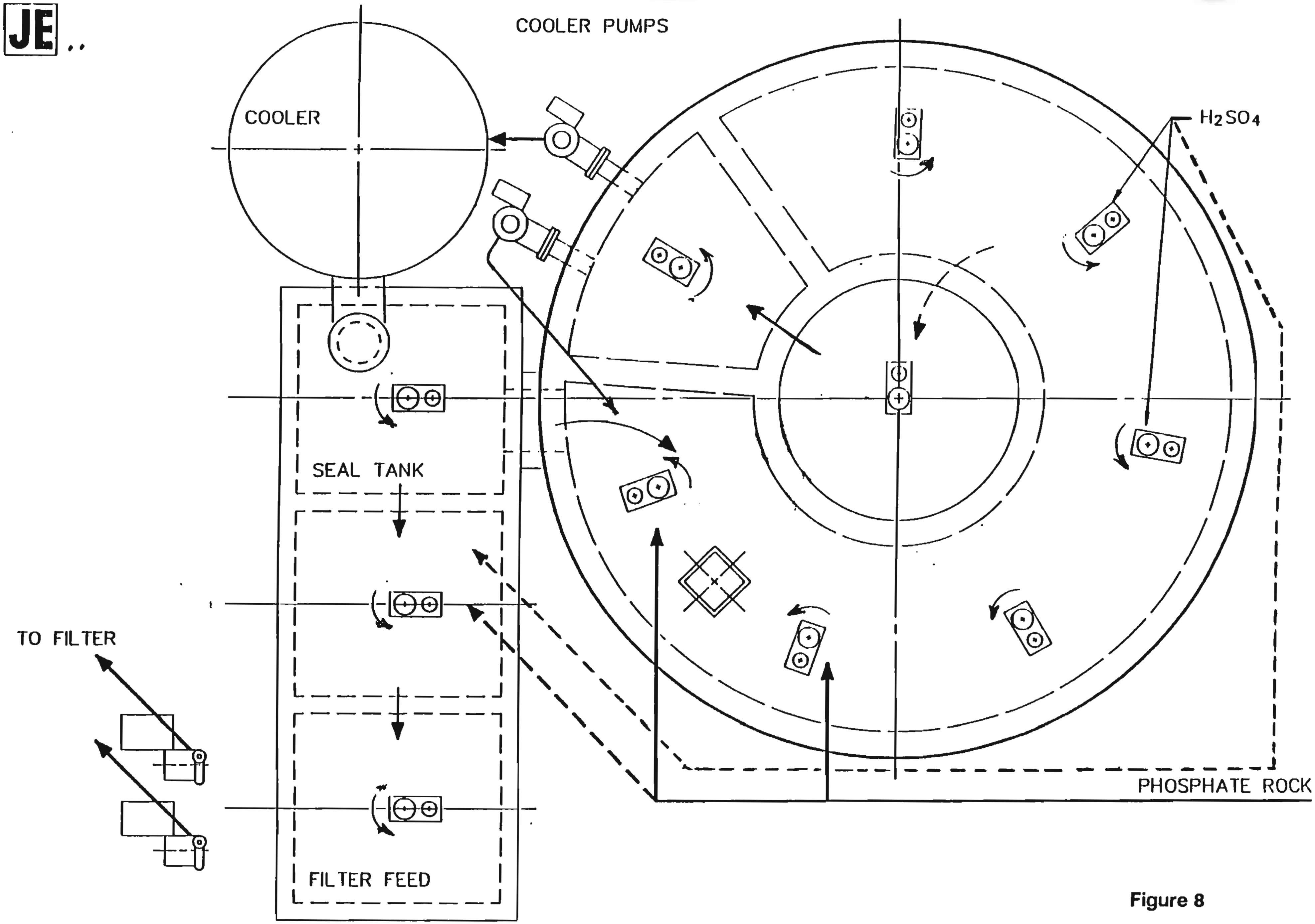


Figure 7

New Cominco Reactor - 1985



JACOBS D II REACTOR SYSTEM

Figure 8

Hubei Projects

large volume of slurry exists to provide a flywheel effect against deviations in sulfate. One of the characteristics of the annular reactor has been stable and easy sulfate control.

Figure 9 is a picture of the recently commissioned Paradeep phosphoric acid plant in India. The configuration is shown in Figure 10. This is a relatively large reaction system by U.S. standards with a total volume of about 1850 m^3 (65,000 CF). The filter is a No. 12 Ucego designed for 900 TPD using any one of 6 different commercial rocks. It has been operating on Togo rock and will operate next on Senegal material. P_2O_5 yields at rates around 1000 MTPD have been above 97%, based on cake samples.

We cite the above three examples as the range of models and accessories available for dihydrate plants to be built in the 90's.

ECONOMIES OF SCALE AND PLANTS FOR THE NINETIES

Over the past two decades, phosphoric acid plants have become larger and larger. It is likely that future plants will continue this trend so that single line plants of 2000 tons P_2O_5 per day, or more, are envisioned. The digestion system for such a design capacity might look, as shown in Figure 11. We are calling this the Jacobs D-2000.

This sketch shows the largest annular reactor yet proposed by Jacobs, about 75' in diameter containing a slurry volume of about 2000 cubic meters (70,000 CF) plus a cooler seal compartment, an adjustment compartment, and a filter feed compartment, each of 200 cubic meters, for a total volume of 2600 cubic meters.

Half of the pumped slurry is circulated through the coolers to lower the filter feed temperature and desupersaturate it prior to filtration. Configurations are also available which put the total flow through the cooler. Jacobs' reactor and cooler arrangements are flexible to meet specific situations and client preferences.

Single filters matching this reactor size are, we are told, on the boards at Bird and Aoustin-Ucego, and multiple filters of any type can be used, of course.

MODIFICATION PROJECTS FOR THE NINETIES

It is probable that most action in the 90's will consist of modifications to existing plants. The most likely plan is to squeeze more out of an existing reactor by adding more cooling and more circulation and to add supplemental filtration and more evaporation.

A typical project of this type was recently completed by Jacobs at the Pocatello, Idaho plant of J.R. Simplot. The project consisted of the addition of a 65 m^2 belt filter and a new evaporator which included a Hastelloy G-30 heat exchanger. The project took about 14 months total and came on line in January 1990.

The new filter brings to three the number of 65 m^2 belt filters operated at that plant. The three handle the entire plant output of over 1200 TPD P_2O_5 from Western rock, the largest existing plant operating entirely on belt filters.

The evaporator is operating as a first stage from 27% to 42% P_2O_5, well above a rated capacity of 700 TPD P_2O_5, handling about two-thirds the plant output.

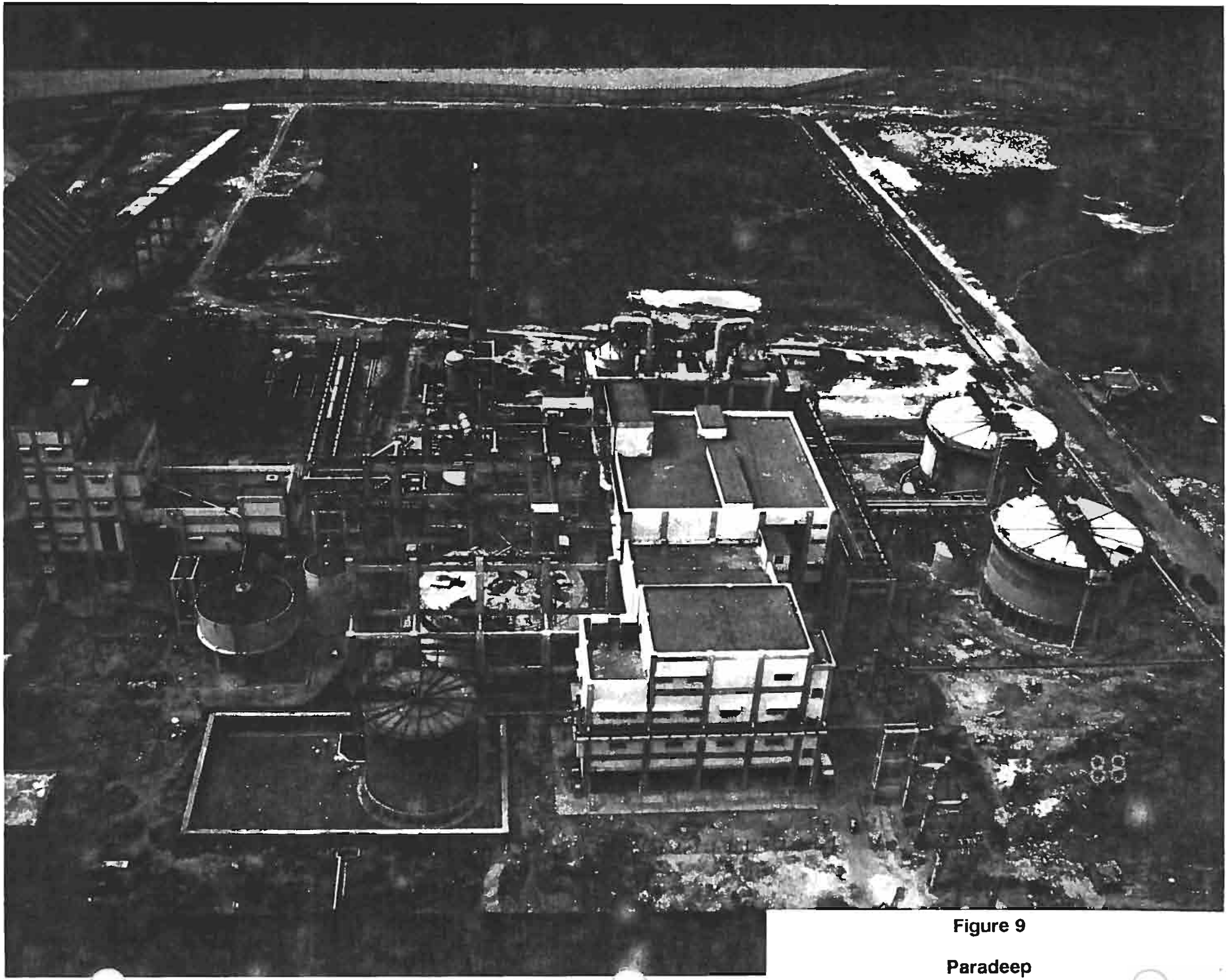


Figure 9

Paradeep

JE JACOBS ENGINEERING GROUP INC.

PN:	TYPICAL JACOBS REACTOR FOR DIHYDRATE PHOSPHORIC ACID PROCESS
Prepared By: S.M.J.	
Date: 7-25-90	
Ref: 0319019A	

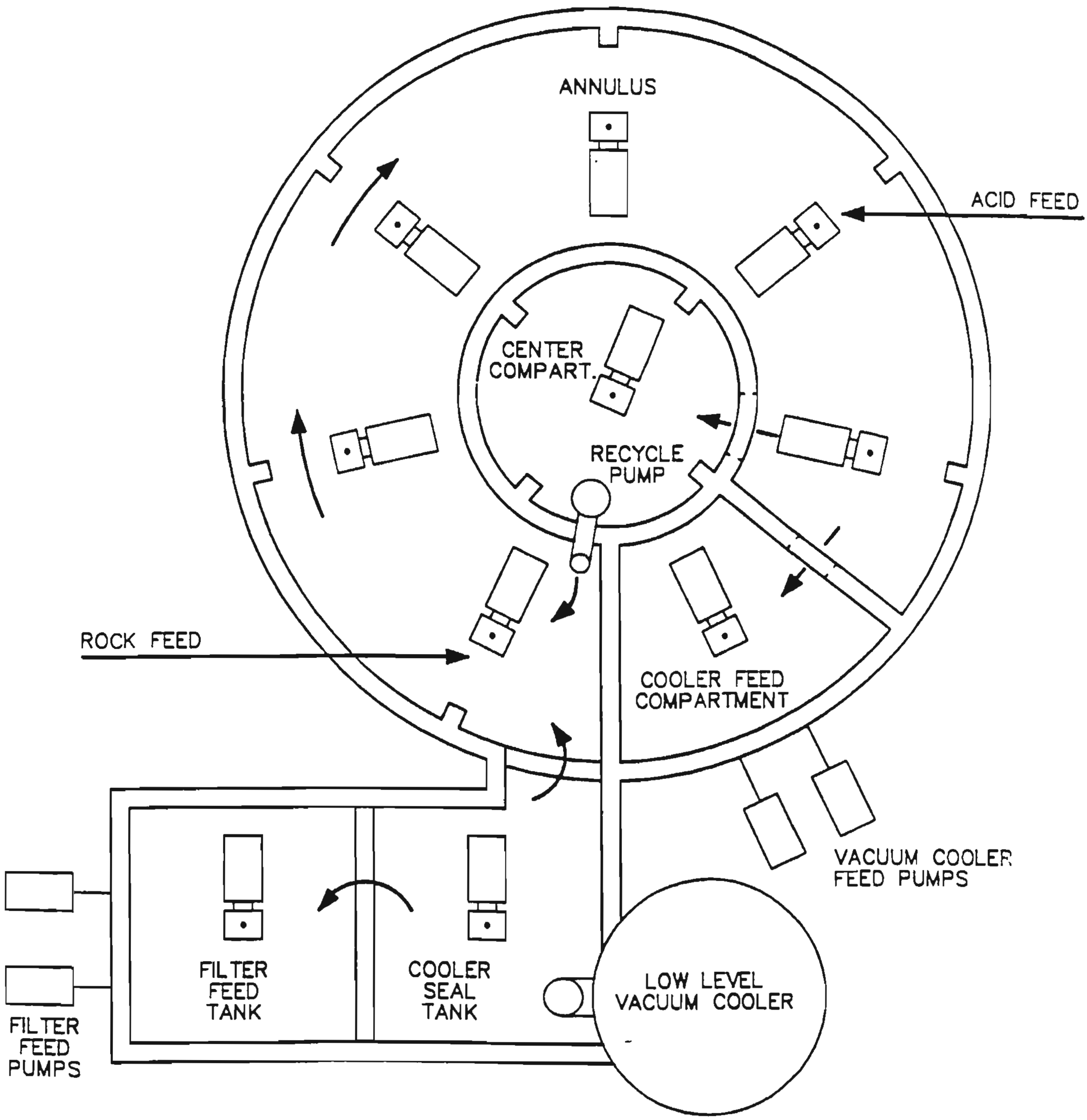
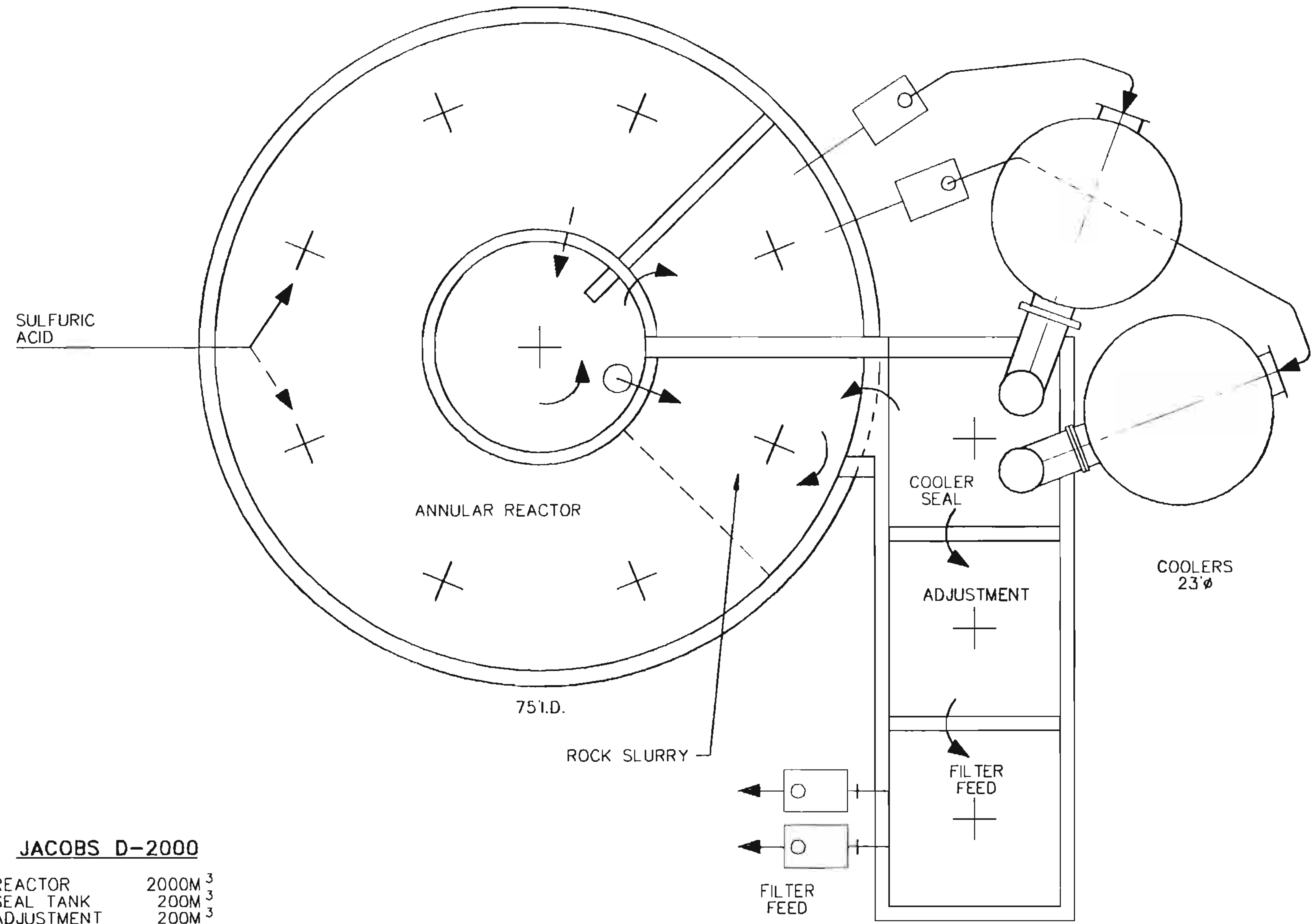


Figure 10

Paradeep Configuration

JACOBS D-2000



JACOBS D-2000

REACTOR	2000M^3
SEAL TANK	200M^3
ADJUSTMENT	200M^3
FILTER FEED	200M^3
TOTAL	2600M^3

FLOW:

TO COOLERS: 36,000 GPM EACH
BY-PASS SLURRY: 72,000 GPM
ΔT @ 2200 STPD: 3.5°C-4.0°C

FIGURE 11

503127A

HEMIHYDRATE IN THE NINETIES

In 1968, shortly before the startup of the first modern hemihydrate-dihydrate plant, using the Dorr HYS process, Bill Weber, Dorr Oliver's phosphoric acid scion, predicted that virtually all future phosphoric acid plants would utilize the hemihydrate process.

Several factors conspired to work against this prediction. Wet rock slurry feed came in the 1970's as one of the major deterrents. Other causes included a slower than expected rise in energy costs, recovery of uranium, the intransigence of established modes of operation, the very large size of demonstrated dihydrate plants, lower filtration rates for a given installation and, in certain cases, higher capital costs. Generally, demonstrated operating factors also have been lower, at least initially due, perhaps, to the complexity and the more severe operating conditions, particularly for the two stage HDH process.

However, several new hemi plants have been built and a significant number of dihydrate plants have been converted to hemi or hemi-dihydrate operation. Table 2 lists the more important of such plants. We see these conversions occurring often where special factors exist, such as, (1) the availability of dry rock (usually imported dry rock), (2) lack of cheap steam as with roaster acid plants, and (3) the requirement to make super acid. Each case needs special examination because the conversion requires a short payout to justify allocation of scarce capital. In plants which use wet rock slurries, such as in Florida and Louisiana, it appears difficult to justify hemi conversion. In China, many phosphoric acid plants will be located adjacent to phosphate mines. Much of the rock requires beneficiation at a relatively fine size so that the most convenient form to handle is a wet slurry of about 65% to 70% solids. The local rocks are also relatively high in impurities. These factors suggest that an appreciable share of China's future production may be via dihydrate.

SUMMARY - THE CRYSTAL BALL

We see a mixed bag, some dihydrate, some hemi-dihydrate and a little straight hemi as the phosphoric acid technology for the remainder of the nineties.

We see, mostly, modification to existing plants as the expansion mode.

We see increased use of belt filters, which may have finally overcome their worst problems. We see even larger tilting pan or table filters; 250 m^2 to 300 m^2 are possible.

We see no really startling breakthroughs. It is possible that at the end of the next 60 years, we will still be using similar technology to that of the last 60 years.

Table 2

Major Hemihydrate Installations

Owner	Location	Year in Operation	Process	Product Acid Strength	Rock	Nominal Capacity MTPD
Windmill	Holland	1970	N-H-(H)	42	Togo/FL	700
Windmill	Holland	1985	N-H(C)(H)	42	Togo/FL	250
Albright & Wilson	UK	1978	N-H(HDH)	42	Mor.	600
SUPRA	Sweden	1988	N-H (C)(HDH)	42	Mor/FL	360
Chinhae	Korea	1990	N-H (C)(HDH)	45	FL	250
Belledune	Canada	1986	N-H (C)(H)	39	FL	500
Arcadian	(USA)	1980	N-H (C)(H)	40	Bou Cra	600
Occidental	Florida	1974	Oxy(H)	38	FL	300
Occidental	Florida	1980	Oxy(H)	38	FL	1400
Gresik	Indonesia	1984	Nissan C(HDH)	42	Jordan	550
Nam Hae	Korea	1988	Nissan C(C)(HDH)	42	FL/Jordan	1100
Yong Nam	Korea	1989	Nissan C(C)(HDH)	42	-	400
Copebras	Brazil	1987	Nissan C(C)(HDH)	-	Brazil	450
Coop Chem.	Japan	1987	Nissan C(HDH)	-	-	230
Zhanjang	China	1993	Oxy(H)	40	China	110
Yunnan	China	1992	N-H(HDH)	45	China	210

NH = Norsk Hydro

(C) = Conversion

(H) = Hemihydrate, Single Stage

(HDH) = Hemihydrate - Dihydrate