OCCIDENTAL'S HEMIHYDRATE PLANTS

MICHAEL B. CAESAR
OCCIDENTAL RESEARCH CORPORATION

HUDSON C. SMITH
OCCIDENTAL CHEMICAL COMPANY

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INTRODUCTION

Occidental recently brought on stream a large hemihydrate process phosphoric acid plant bringing total production to over 1,000,000 TPY P_2O_5 at its White Springs facilities; about half of it by the new process. In view of the interest in the new process, this paper has been prepared to report on the development of the process and on plant design and operations.

PROCESS DEVELOPMENT

In the early 1970's Occidental made commitments to sell over one million tons of P_2O_5 per year, mainly as superphosphoric acid, starting in 1980. When the commitment was initially made, our phosphoric acid capacity at White Springs, Florida was 220,000 TPY P_2O_5. Plans were therefore made to construct new capacity based on the best technology which would remain competitive throughout the 20 year contract.

Many phosphoric acid processes were considered including several existing hemihydrate processes. Although the hemihydrate processes had the obvious advantage of producing high strength acid, resulting in lower energy requirements, none of those reviewed were satisfactory to Occidental. Filtration rates were low and other problems usually associated with hemihydrate had not been adequately overcome. Occidental researchers, who already had extensive experience in developing crystallization processes, initiated a program to develop a hemihydrate process that would satisfy the Occidental criteria. After bench scale and pilot plant work a prototype production plant was designed with a capacity of 350 TPD.

The first expansion, in 1975, was planned to increase the capacity at the original Suwannee River Chemical Complex from 220,000 TPY to 550,000 TPY P_2O_5. This expansion included building a 350 TPD prototype plant. However, since the Occidental hemihydrate process had not been commercially proven, a large conventional dihydrate plant was installed at the same time in order to provide the major portion of the required additional production. The Suwannee River Complex was eventually debottlenecked to provide 660,000 TPY P_2O_5.

A "grass roots" expansion at Swift Creek, in 1979, was made to increase the overall production capacity from 660,000 TPY P_2O_5 to more than 1,000,000 TPY P_2O_5, with the new production capacity providing the bulk of the SPA required for the Russian Project. The importance of this project and the criticality of the phosphoric acid operation to the project required that Occidental produce a high quality acid at minimum cost. The eventual success of the Occidental 350 TPD hemihydrate plant at Suwannee River led to selection of the Occidental hemi process for the 1,433 TPD plant, which came on stream in November, 1979. The selection of the Occidental hemihydrate process, however, was not made until a careful evaluation of some of the best known dihydrate processes was made. Although the operation of the 350 TPD plant at Suwannee River demonstrated that the process was reliable, it still had to be considered as a relatively new process. However, after considering some of the major advantages of the Occidental hemihydrate process listed below, it was felt that the potential risks of a thus relatively new process, were extremely low compared to the potential benefits which could be realized.

1. High strength acid and hence lower energy requirements to evaporate to final shipping concentration.

2. Lower capital costs.

3. Low agitation energy requirements in the reaction vessels.

4. Product acid has low impurities and low solids content.

5. Reduced consumption of sulfuric acid.

6. Proven ability to operate on Occidental's wet unground rock.

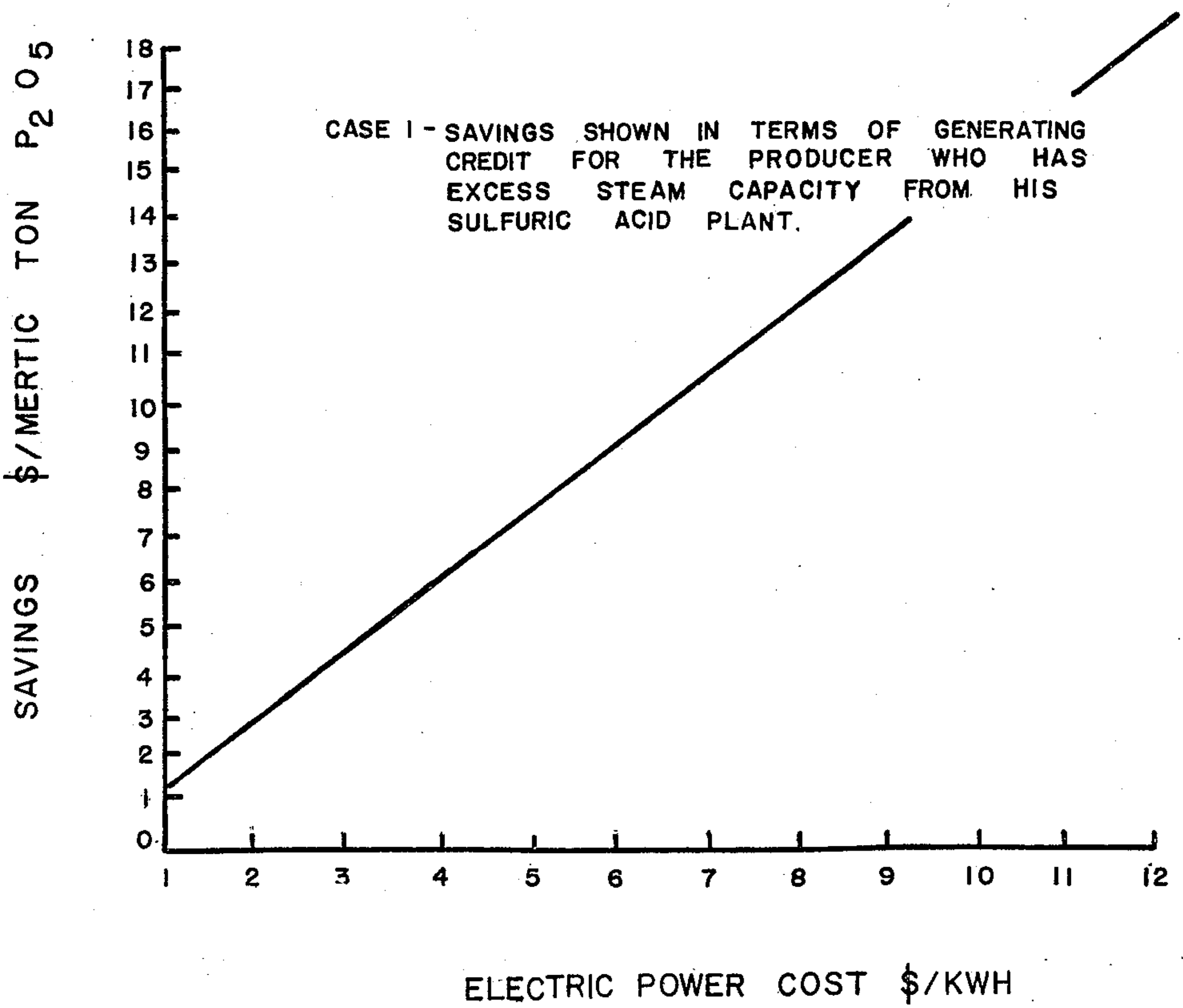
7. Good filtration rates.

Events since the process selection for Swift Creek was made (in May 1978) reinforced the justification for choosing a low energy process. For instance, Figure 1 shows the sensitivity of the cost advantages of the hemihydrate process to the cost of fuel. It is obvious that the cost advantages considered when selecting the process have increased considerably with the recent rapid rise of fuel costs.

Occidental's hemihydrate plants make 38-44% acid directly from wet unground rock. Figure 2 is a simple flow diagram of the reaction system. Rock and recycle acid are mixed in the slurry tank, which is quite strongly agitated and has sufficient retention time to allow much of the carbon dioxide in the rock to be evolved. The still reacting monocal slurry flows by gravity into the second vessel which is a draft tube agitated tank. Rock dissolution is largely completed in this vessel which is called the dissolver.

Slurry is pumped from the dissolver into the crystallizer, a vacuum vessel which is also draft tube agitated. Sulfuric acid is added in this vessel and process heat extracted by vacuum evaporation. Slurry is circulated between the two main reaction vessels at a rate which controls two distinct sulfate levels. From the crystallizer the hemihydrate slurry goes to a filter feed tank, which acts as a process surge tank as well as a utility tank during start-ups and shut-

OPERATING COST SAVINGS ($/METRIC TON P_2O_5) DUE TO THE LOWER STEAM REQUIREMENTS OF THE OXY PROCESS



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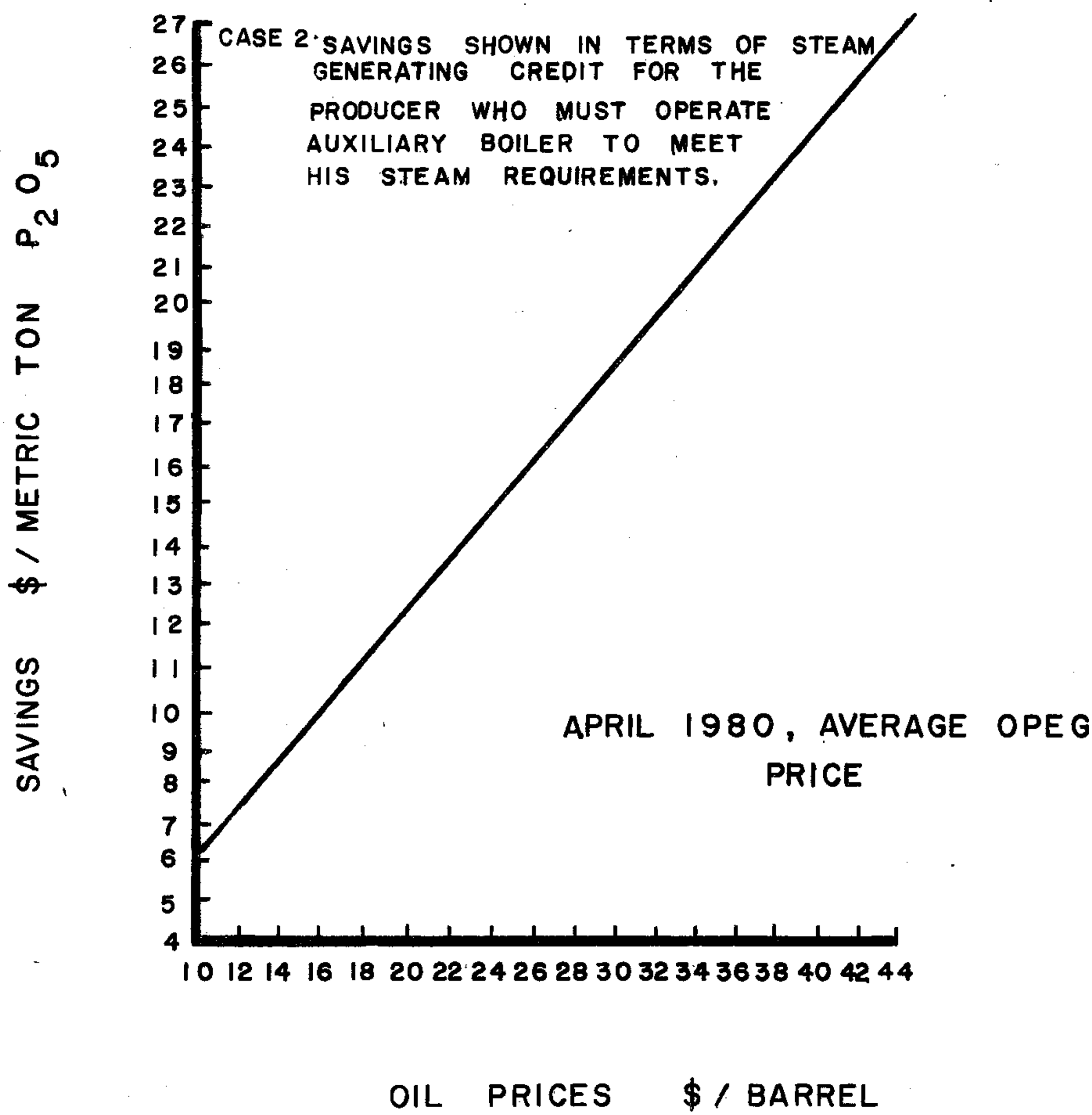

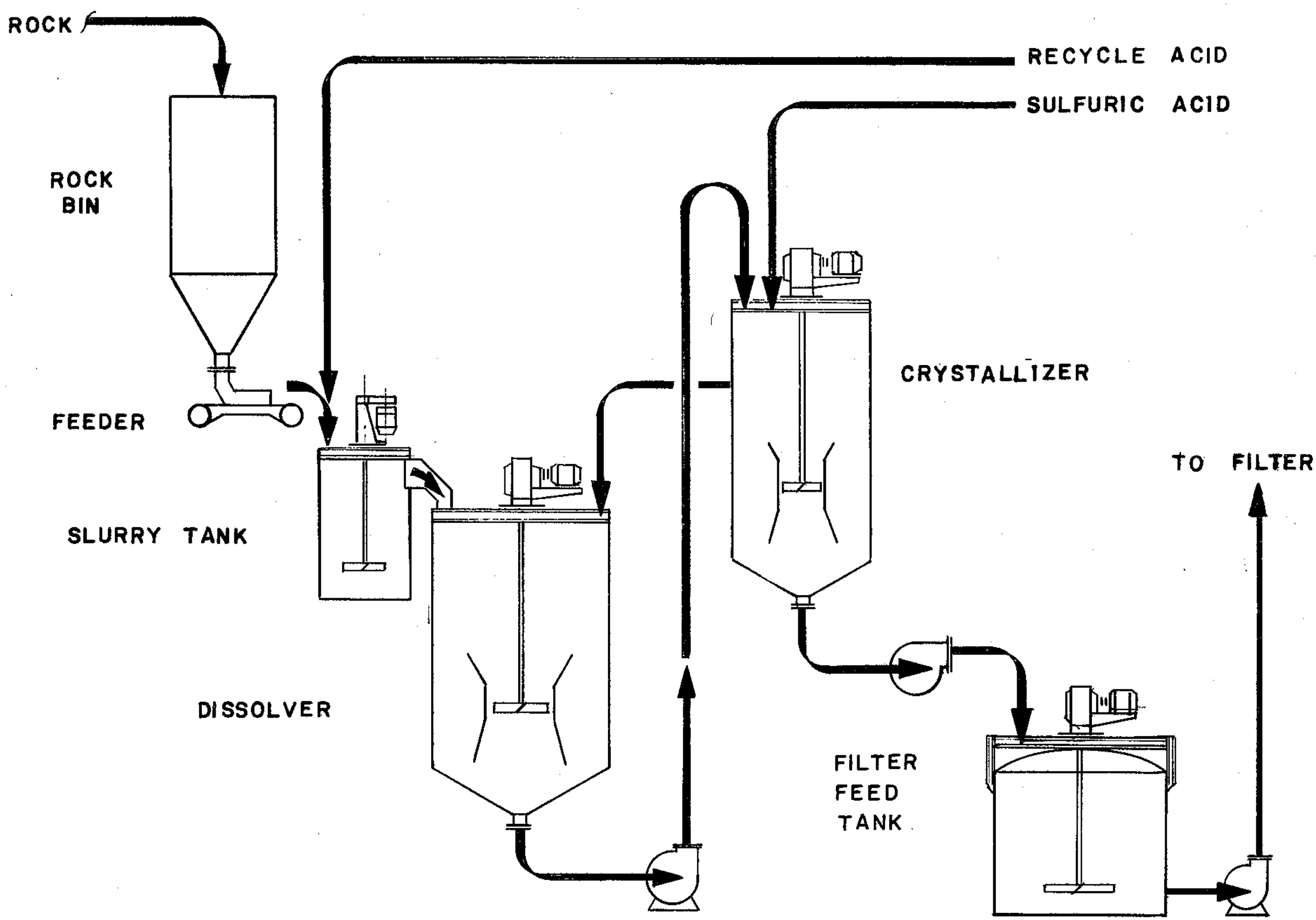

OCCIDENTAL HEMIHYDRATE PROCESS - REACTION SECTION downs. Slurry filtration is conventional, with three countercurrent washes starting with pond water.

The process was developed around fundamental crystallization theory taking into account such variables as crystal habit, size distribution, weight of crystals formed for each set of conditions, the number of crystals formed, and rates of crystal formation and growth. It was soon discovered that highly filterable slurry could be produced with the correct liquid phase parameters, with the correct vessel volume ratios and with crystal habit and population control.

DESIGN CONSIDERATIONS

Most of the early work on the process was done in a one-tenth TPD pilot plant. This size is a convenient step up from bench scale operations without being too large to require heavy equipment. Occidental has two pilot plants of similar size, which are used for testing various rocks and generating information for plant design. Data from the pilot plant showed that scale-up could be based on kinetic data without constraints imposed by geometric and dynamic similarity. This leaves the designer with very wide scope in the choice of vessels, agitators and other equipment, and a clear path to design for economic balance between capital and operating costs. This also means that existing phosphoric acid plants can be converted to the hemihydrate process and much of the existing equipment retained.

The prototype production plant was designed for 350 TPD P_2O_5, i.e. approximately 3,500:1 scale-up from the pilot plant. It was designed to run on unground calcined rock. However, well into the engineering of the plant calcination was abandoned, mainly because of rapidly rising fuel costs. Over the next two years, major improvements were made, primarily involving pumping and agitation equipment. The plant was built with an oversize filter to accommodate possible process improvements and throughput increases. In 1978, the original tilting pan filter was reassigned to the adjacent dihydrate plant and a new smaller table filter was added. The table filter was sized after an intensive investigation of filtration rates during a comprehensive two month plant test in 1977.

When the Swift Creek plant was conceived, the limiting factor for a single train unit was the size of a draft tube agitated vessel, in this case, the dissolver. So the design proceeded with two dissolvers in series, followed by the crystallizer. This concept was checked in the pilot plant and as expected, gave a higher recovery than the single dissolver concept. But, detailed design showed that the two dissolvers in series required a large mass of interconnecting pipework and valves to achieve the necessary flexibility to operate with either dissolver out of service. This situation became more visible on a scale model built as engineering proceeded. At this stage, with some equipment problems still unresolved, and several months into the engineering, the decision was made to change from the single train concept to a simple split train reaction system feeding a single filter.

Each side of the split train is approximately twice the size of the 350 TPD prototype plant. Dissolvers are 35 ft. in diameter, crystallizers 26 ft. The free surface to volume ratios were increased; in the case of the crystallizers, this gives vapor velocities much lower than those in dihydrate process flash coolers and entrainment is correspondingly lower. This increases the attractiveness of fluosilicic acid recovery from the crystallizer vapors. The Swift Creek Ucego filter was purchased before the smaller model at Suwannee River was brought on line, and as it turned out, before the nameplate capacity was finally established. Since the installation of the Size 7 Ucego at Suwannee River, the standard operating rate has gone up to 500 TPD, with 525 TPD being maintained for long periods without the filter limiting throughput. By comparison, the Swift Creek plant is expected to be capable of at least 1,800 TPD on the Size 12 filter, and has operated at rates up to 1,600 TPD.

DESIGN IMPROVEMENTS

The prototype plant at Suwannee River had the first unique problem; it had to run on uncalcined rock although the plant was designed for calcined rock. Consequently, it took a number of modifications and some time before it could be operated satisfactorily. The first main engineering revision was to rework the pump and piping systems that move slurry between reactor vessels. One pump was eliminated entirely by raising the slurry tank above the dissolver. A major problem was selection of a pump that would handle the gaseous crystallizer feed slurry, since gas quantities were not accurately known. Occidental has since developed new methods and mathematics for calculating pressures in aerated slurries, which enabled close specifying of operating conditions for the pumps in the Swift Creek plant. The large size of these pumps, which had never previously been used in aerated slurry duty, made it difficult to predict actual performance. However, the performance of these pumps has been entirely satisfactory in both production size plants.

Selection of materials of construction posed new problems in wet process manufacturing because of the higher temperatures which exceed 200^{o}F. Different conditions in each vessel are taken into account maximum extent possible to avoid interference with construction activities. Concurrently with operator training, maintenance personnel received intensive training on all new types of equipment and reviews of maintenance procedures for equipment similar to that already used by Occidental.

As with all construction schedules, delays are more likely than early completions. In this case, a rainy September caused considerable delays. However, due to a tremendous coordination and scheduling effort, the filter area was put on a water run on November 2, 1979, with the reactor following on November 8. The system was drained, charged with acid, and slurry pumped to the filter on November 11, just nine days after the first piece of equipment was ready for operation.

The first month of operation, using only one reactor, had its share of normal start-up problems, but, the operation was very smooth. Plant rates of up to 900 TPD, more than 25% over design, were achieved. The second reactor was brought on line on December 4. As familiarity with the system was achieved, rates were gradually increased, reaching 1,600 TPD.

Occidental's new Swift Creek Complex is unique in that it was designed to produce SPA as the only phosphate product. Since the Russian embargo Swift Creek has produced merchant acid, by-passing the SPA process. There is no requirement for supplemental steam and the complex generates much of its own electricity, largely made possible by the high strength of hemihydrate acid. The product acid is pumped to one of two agitated storage tanks. Clarification equipment was installed for use prior to evaporation, but is often by-passed because of high clarity of the hemi acid.

Cost savings are realized by the use of wet, unground phosphate rock from the adjacent beneficiation plant. Control of the process, due to moisture variations, has not been a significant problem to date. Hemihydrate gypsum stacking characteristics were also unknown prior to the Swift Creek plant. In fact, the solids dewater much more rapidly than conventional gypsum and provide suitable diking material.

Operation of the pilot plant, and two commercial plants, has demonstrated that the process is simple, reliable, and easy to control. This is attributed to the fact that the operation ranges on key variables (i.e. specific gravities, temperature, SO_4) are wider than for gypsum processes, and the process responds much faster because there is complete control of slurry flows and essentially uniform slurry compostion, with minimum sulfate and temperature gradients in each reaction vessel.

Throughout the plant development of the hemihydrate process, a close working relationship between production people and technical staff was required. A willingness to abandon some long developed operational philosophies was necessary to pursue advanced technologies when specifying materials, and in some cases special fabrication techniques are required. Welding of high grade alloys is one example.

Selection of valves, which are vitally important in bottom draw-off vessels, is another special subject. The Swift Creek plant has six special power operated ball valves, up to 16 inch nominal size. The valve problem on the Suwannee River plant was not completely resolved when the Swift Creek plant was being designed, and final selection of these valves took more time than any other item. The 12 and 16 inch diameter valves which were selected have proven to be a very easy operating and dependable valve. Special piping arrangements were also utilized to eliminate solids deposits in the lines so large butterfly valves could be used in slurry service.

Another problem introduced by bottom draw-off vessels is to prevent lumps entering lines and pumps. Occidental designed special "rock boxes" to overcome the problem, and those have been very successful. A patent application is pending on the "rock box".

A Ucego filter was selected for both retrofit of the 350 TPD plant and initial installation in the 1,430 TPD plant because of the ability to wash through the filter cloth, and because of mechanical simplicity. Within a few weeks of the start-up of the Size 7 Ucego, a number of modifications were made to improve operation and reduce the required cleaning cycle. These modifications were concurrently designed into the Size 12 Ucego and have proven beneficial.

In addition, modifications were continually incorporated into the design as information became available throughout the engineering phase of the 1,433 TPD plant. Most recent design changes consisted of instrumentation changes, different materials of construction, evaluation of fume collection points for scrubber loading, and duct sizing and modifications to the filtrate system.

Design of the vessels and draft tube agitators for the two different slurries required exceptionally close coordination between the vessel and agitator designers and the process engineer. Everyone associated with phosphoric acid production knows the importance of proper agitation in the attack tanks; our process is no exception. However, the fact that each vessel requires only one agitator and the horsepower input is relatively low minimizes potential problems. Occidental gained enough technological know-how on the prototype plant to overcome the major design problems, and the Swift Creek vessels have performed to expectations.

Three U.S. patents*, and many foreign patents have been issued on the process and special equipment designed for the process; many other patent applications are pending. The patented entrainment separator, used in vacuum service on the crystallizer and the table filter has proven effective and reliable.

* U. S. Patents 4,132,760 - 4,140,748 and 4,164,398.

SCHEDULE AND CONSTRUCTION

The 1978-1979 expansion of Occidental's White Springs facilities, to satisfy the requirements of the Russian trade agreement, was the result of four years of planning, engineering, and construction. Project scope, financial justifications, and contractor selection was accomplished from December, 1975, to April, 1977. Many alternates were considered during this time period, including site and process selection. Engineering began at a rapid pace in April, and by August, 1977, construction forces moved into the field for the Suwannee River Complex expansion. During this period of time, extensive evaluation of the prototype hemihydrate plant was carried out to determine the feasibility of the hemihydrate process for the Swift Creek Complex. Many design improvements, later incorporated into the 1,430 TPD plant, were made during this evaluation. The first part of this expansion (SPA facilities) was brought on line in October, 1978, and the new Ucego filter for the 350 TPD plant came into operation two months later.

Engineering for the second phase of the SPA expansion (Swift Creek Complex) began in April, 1978. In July, it was decided that the single crystallizer concept for the hemihydrate reaction section was too cumbersome. At this time the entire reaction section was redesigned with two crystallizers, resulting in parallel reaction trains from the rock feeders to the filter feed tank. Because of delays in environmental permitting, field mobilization did not begin until October. Pre-start-up inspections and operations organization began in May, 1979, and the first product was made in November. By December, exactly four years after the project became active, all facilities were on line and construction forces withdrawn.

In order to meet the ambitious schedule, it was necessary to use as many expedient engineering and construction procedures as possible. The Occidental Project Team was formed with persons having both operations and engineering experience. The Project Team members were delegated maximum authority to hold engineering approval times to a minimum. A task force approach to engineering was used, with all design disciplines, project engineers, and administrative support personnel working side-by-side, with no other projects detracting from the Occidental project. Conceptual and detail design models were used extensively. As systems were designed, they were immediately incorporated into the model, thereby greatly assisting coordination efforts between the various engineering disciplines.

Efficient purchasing and construction procedures were employed to enable a "grass roots" plant to be constructed in one year. Of prime importance was a project agreement which provided for a no strike clause, make-up days, and a four day work week. Purchasing time was minimized by unit pricing for the duration of the project for bulk items, splitting orders for best delivery, earliest possible commitment of orders, and intensive expediting and inspection. Rapid construction efforts included optimum plant layout, on-site engineering and procurement coordination, and a cost plus fee electrical subcontract. The project was within budget in spite of the accelerated schedule. Start-up was basically trouble free because of client operational involvement in design and construction.

OPERATIONS

350 TPD Prototype Plant

The prototype plant was conclusively demonstrated in a special two month test in 1977. Details of this test were published in a paper delivered to the British Sulfur Institute in November, 1979. Following the test, there were some mechanical problems still unresolved and intensive work in the first few months of 1978 led to modifications that overcame these difficulties. 1979 was the first full year of dedicated production for this plant and it achieved 95% of its production goal. During 1979, the maximum instantaneous rate was increased to 525 TPD. Most of the production from this plant goes into granular products, without any further treatment other than passing through a raked surge tank. Hemi acid is highly successful in the granular plants because of its lower impurities, enabling better grade control and longer clean-out cycles.

1,430 TPD Swift Creek Plant

The start-up of the 1,430 TPD plant at Swift Creek was much more involved than the 350 TPD plant, since it was the heart of a "grass roots" plant. Coordination with other battery limits units and supporting utilities required constant revised estimates of a start-up date for planning purposes. Finally with an October, 1979, start-up predicted, supervisory personnel were selected in July and trained in the process details and supervisory fundamentals. Operators were selected in August and were given a general course in operating fundamentals, process details, and intensive training on the digital instrumentation system that was selected for use throughout the Swift Creek Complex.

After approximately six weeks of formal training, in-plant familiarization and reviews of the specific duties of each job were conducted by the first line supervisors. Nights and weekends were used to the required for hemihydrate operation. Occidental has come a long way, since the first plant started up in 1975, in developing the new techniques that make it possible to achieve the benefits of the hemihydrate process. Occidental's 350 TPD plant, the largest hemihydrate unit of its time, was a daring innovation in the mid seventies. Its 1,433 TPD plant is the forerunner of wet process technology for the eighties.