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UPRATE OF THE ZIMPHOS PHOSPHORIC ACID UNIT IN ZIMBABWE

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IN ZIMBABWE

1 INTRODUCTION

ZimPhos is a major fertilizer company in Zimbabwe, Southern Africa, owned by Chemplex, a holding company operating both a local phosphate rock mine and the ZimPhos plant converting the rock into phosphoric acid and fertilizers. This plant includes among other products the manufacture of sulfuric and phosphoric acid and low grade NPK fertilizers by steam granulation of dry raw materials with ammonium nitrate.

With a growing demand in high-grade fertilizers, Chemplex decided to uprate and modernize its old phosphoric acid unit to increase the capacity and cut the production costs, with an ultimate aim to produce fertilizers based on ammonium phosphates.

In October 1995, ZIMPHOS awarded a contract for modernizing and increasing the phosphoric acid capacity from 20,000 up to 40,000 mtpa P2O5. Michel BARLOY, who was in charge of the implementation of the project, developed the process technology used in the revamp. KEMWorks Technology, Inc. of Lakeland, Florida provided assistance in procurement of special equipment and project coordination.

This paper was written in January 1997 prior to the commissioning scheduled in March. The results and performances of the uprated unit are discussed in an appended section prepared in April 1997 during the start-up. In this paper, subjects mainly of interest for the US phosphate industry are mentioned.

2 RAW MATERIALS

The igneous phosphate rock is mined and beneficiated about 265 km from the ZimPhos plant and is transported by rail cars. With a granulometry of 100 % below 32 mesh (500 μ) and 90 % below 60 mesh (250 μ), it does not need grinding for phosphoric acid manufacture. The rock analysis on dry basis is as follows:

P2O5	:	35.50
CaO	:	50.00
CO2	:	2.50
SO3	:	0.05
F	:	1.60
SiO2	:	5.40
Fe2O3	:	1.26
Al2O3	:	0.60
MgO	:	1.28
Na2O	:	0.76
K2O	:	0.08
C org.	:	0.10

Before the uprate, the gypsum crystals produced with this rock quality were thin and needle shaped with poor filtration characteristics.

The 98 % H_2SO_4 produced in a pyrite burning plant was diluted to 70 % before introduction in the reactor tank.

3 THE PHOSACID UNIT BEFORE UPRATE

The Prayon unit commissioned in 1958 was probably the oldest unit still in operation in the world and is a testimony of the durability of this technology. The nominal design capacity was 40 mtpd P_2O_5. Before the uprate, the instantaneous capacity on 24 hours basis was 80 mtpd, but due to a low on-stream factor, the maximum capacity achieved in a calendar year was hardly 18,000 tons P_2O_5.

The reaction system included 2 circular reactor tanks each divided into 4 cells, with a total working volume of 135 m3. 140 m3/h of slurry was recirculated from cell 6 to cell 1 through the vacuum cooler located on the building roof, while cells 7 and 8 were used for desupersaturating the slurry before filtration. The reactor tanks are located on the upper floor of the building, and the pan filter was fed by overflow from the last cell.

The original Prayon filter of 15-m2 active area was still in service with many of its original parts after nearly 40 years operation. The filtration section of conventional Prayon design naturally included a seal tank.

The evaporation unit is conventional and was built in the 70's to replace the original submerged combustion unit. Part of the concentrated acid is de-fluorinated with soda ash for manufacturing feed grade phosphates.

Two acidic cooling towers were used to cool down the water from the condensers, the gas scrubber and the superphosphate den.

After the uprate, there is little left of the previous equipment: the rock feed, the shells of the reactor tanks, the bottom and the top of the vacuum cooler, the vacuum cooler condenser and the gas scrubber.

4 NEW REACTION SYSTEM (See attached flowsheet)

a) Attack and crystallization cells

In order to increase the reaction volume from 135 to 180 m3, the 8 cells are used for the rock attack and gypsum crystallization by putting the intake of the new slurry pumps on cell 8. Cells 1 & 2 are assigned the rock attack and cells 3 to 8 the growing of gypsum crystals.

All agitators are replaced by new ones from Missenard-Quint (France). They are all the same except the motors of 22 kW in cells 1 & 2 and 15 kW in cells 3 to 8, and different rpm accordingly. The agitators have one airfoil impeller designed for an optimum balance of power between flow and shear, and one turbine of smaller diameter close to the bottom for preventing the gypsum from blocking the cell underflows. This is required by the higher circulation rate.

From the last cell (# 8), the slurry overflows to the new digester with no slurry level control.

b) Slurry recirculation and sulfuric acid distribution

In many units all the slurry circulation goes to the vacuum cooler although it has 3 independent functions: cooling the slurry with a low δT; mixing the raw materials with enough desupersaturated acid for limiting the supersaturation and the formation of many small nuclei; and, importing the sulfuric acid needed for digesting the rock. Each function has its own slurry flow requirement, which cannot be met with a single flow. Moreover, the flow is generally constant and cannot change with the rock rate to meet the optimum conditions of operation.

The new recirculation system can be considered as ideal for optimizing at any time the crystallization regardless of the rock rate:

- Part of the slurry is recirculated through the vacuum cooler with a pump fitted with a variable speed frequency motor. Average flow: 140 m3/h (620 gpm).
- Another part of the slurry is independently recirculated from cell 8 to cell 1 with another pump also driven with a variable speed motor. Average flow : 500 m3/h (2200 gpm)
- Because the sulfuric acid feed is introduced in the vacuum cooler, the slurry returned from there goes first to a seal tank from where it is distributed by overflow in any proportion to any of the cells 1 to 4. That means the sulfate can be individually adjusted to the optimum value in each of these cells regardless the slurry circulation rate.

Every parameter can therefore be adjusted independently from the other ones. In order to optimize the slurry flow and the sulfate level in each cell, a simple filtration test is used and gives relative results (filtration time corrected to a reference cake thickness) for comparing the change in filtration rate when changing the operating conditions. From there, instructions are given to the operators to set the slurry flows and distribution according to the rock rate and other operating parameters.

c) Vacuum cooler and sulfuric acid introduction

The heat load in the vacuum cooler is increased because the rock feed rate is almost doubled, sulfuric acid is no longer diluted and there is no increase in the air cooling system. To minimize the cost of the modifications, only the middle part of the vacuum cooler is replaced by a new one of same height, but larger diameter (2.6 m = 8.5').

The main innovation is the acid mixer in the vapor body of the vacuum cooler. Sulfuric acid feed in a vacuum cooler is not a new concept. Singmaster & Breyer introduced it in the early 60's and the idea has surprisingly not been picked up by other licensors. In those units, the vacuum cooler had a slurry agitator at the bottom where diluted sulfuric acid was introduced. Some of these vacuum coolers are still used in Mississippi and Idaho, with modifications made by the users. A similar system has been used successfully in France with the acid mixer on top, not in the slurry. The ZimPhos technology is improved in two ways:

- The acid mixer is designed for an intimate blend of sulfuric and phosphoric acids in the space, not in the liquid. The advantages are obvious: the dispersion and the blending effect are much faster, and the blend is already cooled down and diluted before touching the slurry, thereby reducing the local supersaturation with no chance of making hemihydrate crystals.

- The mixer design prevents any contact between the acid blend and the construction materials, thereby avoiding scaling and corrosion. It is already used successfully in the gas space of reactor tanks in several phosacid units, including in the U.S. Different modes of realization will be tested in the ZimPhos unit for optimization.

- There is no slurry hold up at the vacuum cooler bottom, which is an advantage because the slurry has a relatively high sulfate level.

The slurry recirculation through the vacuum cooler is needed more to prevent scaling the vacuum cooler bottom and the tail pipe than for cooling the slurry itself, although some cooling is needed. Indeed, as a rough order of magnitude, diluting the sulfuric acid generates two third of the heat to be released from the system, while the original Prayon design intended to release one third of the heat to the scrubber. Most of the heat removed from the vacuum cooler is coming from the acid blend in the mid-section of the vacuum cooler body, which justifies not changing the bottom part.

As regards the materials, the clone vacuum cooler was totally carbon bricklined except on the top. In ZimPhos plant, the new middle section is lined with rubber plus Hypalon that can stand splashes of hot concentrated sulfuric acid. However, the spray pattern of phosphoric acid out of the mixer prevents the sulfuric acid to reach the vacuum cooler lining, which was checked by water test.

d) Vacuum cooler condensers

The existing condenser is kept unchanged except for larger spray nozzles to meet the increased water flow rate requirement. The diameter of the tail leg is not changed in an attempt to get enough vacuum without using a vacuum pump.

The vertical duct linking the top of the vacuum cooler to the condenser is converted as a pre-condenser with 3 objectives: to increase the condensing capacity, to get hot water for washing the gypsum on the filter and to recover any possible carry-over of acid from the evaporator.

e) Digester

A new digester of 90 m3 (50 % of the reaction/crystallisation volume) is installed at the ground floor level. A digester is advisable for cooling down and desupersaturating the acid while slightly increasing the gypsum crystal size. There is a provision for a small sulfuric acid addition to still decrease the supersaturation. The digester is an easy and cheap way to increase the overall reaction volume because it is made in rubberlined carbon steel with only the bottom bricklined. This is possible because the agitation is gentle just for keeping the homogeneity of the slurry. The Missenard-Quint agitator driven by a 30 kW motor has an air foil impeller and a bottom turbine.

f) Filter feed

From the digester, the slurry overflows to the suction of a self-control pump, thereby keeping a constant slurry level with no need for adjustment. The filter feed is steadier than with a manual or automatic level control, which increases the filter capacity and facilitates the control of the operating parameters.

5 NEW FILTRATION SECTION

The original Prayon pan filter was too old in design and equipment to be economically rebuilt. Moreover a belt filter is more suitable for a small filtration area. A Philippe belt filter (France) of 25 m2 has been installed close to the old one. It may look oversized, but savings on better performance of the unit always quickly pay back the additional cost of an oversized filter. With an active dimension of the belt of 2.5m x 10m, the filter has been specifically designed to be erected in an available space of the building.

The specifications of the filtration section are:

a) There are 2 washes instead of 3 on the former filter thanks to the straight use of 98 % sulfuric acid.

b) There is no seal tank although the filter is at high elevation required by the space and floor available. The tail legs are connected to the suction of self-control filtrate pumps. This is not a new concept since there are many filtration units like this one in the world, included in the U.S.A. The main advantages have been described in a previous AIChE paper, one of them being the savings on investment particularly in decreasing the building cost.

c) What is entirely new is the absence of filtrate receivers. The separation of gas and liquid is made by T connections with low enough velocities to have little carry-over. One advantage in a new layout is to still decrease the filter elevation, which is governed by the point of separation between liquid and gas.

d) The product acid goes by gravity to the storage tank, which is at a lower elevation than the filter.

e) There is a small port at the end of the third filtrate in the vacuum box for collecting the tail of the third filtrate. The flow is measured and set at a value corresponding to a minimum P2O5 loss. The filter speed is monitored by the flow, which is automatically maintained at the set value.

f) The stationary part of the vacuum pump (supplied by Alsthom, France) is rubberlined to stand the corrosive pond water feed without using an expensive 316L material. There are a few references for pumps in this material in the phosphoric acid industry, and much more in the sugar industry despite gravel particles coming in the pumps. The rubberlining has to be checked every year for possible but unlikely repair of the rubber, which can be easily done.

g) An important feature of the filtration section design is the switch from operation to wash and reverse with no dead time just by opening and closing two couples of valves. That keeps the filter clean and increases the on-stream factor.

6 EVAPORATION

6.1 Equipment modification

The major change is the replacement of the heat exchanger by a larger one with wrapped tubes from Sigri (Germany). Other minor modifications have already been done without waiting for changing the heat exchanger:

- The condenser had a water chamber with a perforated plate fitted with ceramic nozzles on the holes. The nozzles had to be cleaned every week. After removing them, the vacuum did not change, and the plain holes do not need cleaning anymore.

- The steam valves on the steam ejectors have been closed with no change in vacuum.

- The production tail pipe has been connected straight to the pump suction instead of going first in a seal tank. The latter is not removed because it is still used for sealing the leg of the droplet separator as a mean to check the amount of any possible carry-over.

- The acid level in the flash chamber is lowered by 1300 mm and is now at the bottom part of the circulation pipe. The issue is to decrease the hold-up for less dead time in draining the liquid before and after the heat exchanger wash. The chance was an increase or decrease of carry-over, and the risk was to scale the void part of the flash chamber by flashing the incoming recirculated acid. No carry-over and scaling has been observed.

Other improvements made along with the change of the heat exchanger are:

- In order to minimize the water leak in the acid through the mechanical seal of the circulation pump, the water pressure at the outlet pipe is set and controlled at a value slightly higher than the acid pressure.

- To still increase the vacuum in the condenser, the diameter of the tail leg has been decreased. The new velocity is 4.2 m/s (13.8 ft/s) based on gas free water gravity. To cope with the pressure drop, the tail leg is directly connected to the suction of a pump with no seal tank.

6.2 Control of the acid concentration

There were two options for controlling the acid boiling temperature and thereby the acid strength:

a) To set the feed acid at a constant flow and to control the steam pressure (or temperature) to keep steady the acid boiling temperature in the flash chamber. After a wash, the feed is set for a steam temperature of typically 110°C (230 °F). As the heat exchanger scales up, the steam temperature rises automatically. When it reaches a critical value as regards the scaling, for example 120 °C (248 °F), the heat exchanger is washed.

b) To set the steam at a constant pressure (or temperature) and to control the feed to keep steady the acid boiling temperature. As the heat exchanger scales up, the feed rate decreases automatically. When it has dropped to a specific value meaning the heat exchanger has scaled to a critical point, the heat exchanger is washed.

Method (a) has the advantage of knowing exactly from experience when the heat exchanger has to be washed. It has the inconvenience of not using permanently the heat exchanger at its maximum capacity. The inconvenience of method (b) is the difficulty to determine at what drop of the feed rate it is safe to wash the heat exchanger.

In the ZimPhos revamp, method (a) is used to be on the safe side as regards the heat exchanger scaling and repair.

7 GYPSUM DISPOSAL AND WATER CIRCULATION

The gypsum slurry is sent to a gypsum stack on a hill at 1200 m from the unit, with a possibility to divert part of it to a nearby plant manufacturing plasterboard. The peculiarity of the gypsum stack is the method to build the dams: the storage area is surrounded by the elevated gypsum line having holes underneath and supported by poles. The slurry is sprayed through the holes, the dam builds up and the water gathers at the center of the stack. Originally, this method was used to avoid a soft wall at the opposite corner of the local slurry feed, but it has the other advantage of no drying time needed when the dam has to be made with a bulldozer. When the stack height has increased to an elevation close to the gypsum distribution pipe, the pipe is raised on new poles as well as the center pit collecting the water. The water was previously returned to a neutralization unit before being recycled to the phosacid unit and other usage.

The whole water recirculation has been redesigned in a comprehensive way to minimize the blow-down of liquid effluents occurring when the rainfall exceeds the seepage and evaporation. The main modifications of the previous system are:

- A new acidic cooling tower is replacing the two old ones.
- The water returned from the gyp stack and pond to the phosacid unit is no longer neutralized, which increases the P2O5 yield and reduces the chemical consumption. Only the water used in other units or sent to the blow-down is now neutralized.
- A single gypsum slurry pump of 10 bar (145 psi) is replacing the two former pumps in series.

8 CONTROL

All process information are now in a SCADA (DCS) system, including the free sulfate and acid gravity control. The free sulfate software automatically reset the sulfuric acid flow to bring the free sulfate level back to the target at the next sampling time. It can detect the start of rock coating and uses a specific procedure to stop it immediately. It recalculates the acid to rock ratio from the previous sulfate results and displays graphs of the last 48 hours results.

A large use is made of self-control pumps, particularly on the tail legs and on the slurry feed to the filter. Self-control pumps automatically offset a flow variation by a change of the liquid level in the suction pipe. A flat TDH versus flow curve and a low NPSH allows a large range of flow within a narrow range of geometric suction height.

9 INITIAL OPERATIONS OF THE UPRATED PHOSACID UNIT

9.1 COMMISSIONING

The phosacid unit was tested with water in mid-March 1997, but a problem appeared immediately with the new FRP pipes (about 80 % of the new piping network) which were leaking. The local pipe manufacturer had used a wrong resin quality making the pipes brittle and not standing the liquid pressure.

It was decided to replace the FRP pipes by locally made polyethylene pipes. A US expert (Bill Shelton from METRO, Pascagoula, Mississippi) came on short notice for giving advice and preparing the basic design of routing and support of the new PE pipes. In the meantime, rubber hoses replaced some FRP lines, and the other ones repaired and reinforced. The operation with phosphate rock started in mid-April, first discontinuously due to a problem of water supply and gypsum disposal. By the end of April, the unit was in industrial operation although the HDPE pipes were not yet installed.

The digester is not yet installed because it can be constructed only after the old filtration section is removed.

9.2 SULFURIC ACID DISTRIBUTION

The acid mixer is working perfectly well with no problem. The slurry from the vacuum cooler containing the sulfuric acid feed is returned in equal quantity to cells 1, 2, or 3 of the reactor tank. There is a provision to return it also to cell 4, but the overflow pipe from the slurry seal tank is not yet installed. Typically, the temperatures are 80°C (176°F) in the vacuum cooler in, 76°C (169°F) in the vacuum cooler return, 81°C (178°F) in cell 8.

9.3 SLURRY FEED TO FILTER

With no digester, the slurry overflows straight to the suction of the slurry pump on the ground floor without any need to control the slurry level in the reactor tanks. The slurry flow is steady and evenly distributed on the filter despite the fact that the slurry is dewatered on less than 1 meter (3 ft) of filter length.

When the raw materials feed is stopped, the slurry overflow is drained for a few minutes to the filter, and then the knife valve at the reactor overflow is closed.

9.4 FILTRATION SECTION

The filtration design without seal tank, product acid pump, and filtrate receivers works well. There has been no need for any adjustment. The wash system with the vacuum box and all ancillary equipment fully flooded has given no problem.

9.5 VACUUM

Due to air leaks on the vacuum cooler lines, the old vacuum pump has been reused, but even with this pump, the vacuum has been a limiting factor for the rock rate. When the leaks are eliminated, the vacuum pump will be put out of service. The vacuum cooler itself is not a bottleneck, and no carry-over of sulfuric or phosphoric acid has been observed in the water pre-condenser.

9.6 EVAPORATION UNIT

The condenser tail leg achieves enough vacuum with no need of the old steam ejectors. It has been noted on both condensers of vacuum cooler and evaporation that a maximum vacuum is achieved with an optimum, not maximum water flow. It seems the top of the legs should have a larger diameter than at the bottom. Investigations are made in this respect. The transparency of the FRP legs is helping the study.

Another interesting modification is the replacement of the heavy sophisticated outside overflow existing on most of the evaporation units by a simple overflow pipe going straight to the production pump with no seal tank.

9.7 RESULTS

The target was to achieve 75 % (105 mtpd P2O5) of the design capacity (140 mtpd P2O5) without the digester. This capacity has been easily achieved at low filter speed (cake thickness 60 to 80 mm), but not much more due to the vacuum pump bottleneck. The design capacity is likely to be achieved without digester as regards the filter capacity.

The P2O5 strength can be maintained around 30 % and has even risen to 32 % with no major degradation of the filtration. There is no measurable dilution from the filter. In the old plant, the product acid strength was close to 27 %.

The P2O5 recovery on the gypsum cake is over 96 %.

In the old plant, the gypsum crystals were small needles with a ratio width to length of 12 and about 20 microns length with many nuclei. In the new plant, the crystals are larger and bigger: ratio of 6 and length of 30 to 50 microns with few nuclei. More amazing is the stability of the plant and the insensitivity to mal-operation. At the start-up, due to wrong calibration of instruments, the unit has been operated during 5 hours with a free sulfate between 8 and 9 % with no sign of hemihydrate and with the filter quite dry. This is due to the excellent dilution and cooling of sulfuric acid before contact with the slurry.

9.8 POINTS TO BE IMPROVED

Process-wise, the results are as good or better than expected, but they have still to be optimized in using the many variable parameters which have been provided: slurry recirculation rate on each pump, sulfuric acid distribution in the first 4 cells.

The new imported equipment items are so far quite satisfactory, but some of the old or local equipment has to be improved to limit the number of shutdowns.

The main problem experienced is some difficulties for draining the seal tanks before washing due to build up choking the knife valves. These valves will probably have to be replaced by plugs.

9.9 ACHIEVEMENTS

The upgraded ZimPhos phosacid unit has successfully tested and proved some innovative design features which are of interest to USA phosacid industry:

- Blending and spraying the sulfuric acid at the top of a conventional vacuum cooler.
- Adjusting the sulfuric acid feed in any of the first 4 cells in normal operation.
- Recirculating independently and at adjustable rate the slurry to the vacuum cooler and throughout the reaction system.
- Overflowing the slurry to the filter from a Prayon reactor.
- Operating a belt filter with T connections instead of filtrate receivers and with no seal tank.

Zimphos Plant

Simplified Process Flowsheet