Phosphoric Acid Plant Cooling Water Treatment Process

Hatch is investigating the development of an innovative Proprietary Process for treating condensed water vapor containing fluoride compounds (1 to 3 % fluoride) as an integral part of the comprehensive Phosphoric Acid Plant Sustainability. The innovative process is used to recover high quality water and commercial strength hydrofluorosilicic acid (20 to 25% FSA). The high quality water suitable discharge can be used as makeup to the Cooling Tower reducing proportionately the amount of fresh water makeup and subsequent cooling tower blow down.

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Abstract

In order to address concerns associated with the financial liability for the final closure of a Phosphate Fertilizer Facility and the ultimate disposition of the cooling pond, Hatch has evaluated the use of Series Filtration (Double Filtration) of phosphogypsum and a Closed Loop Cooling Water System as an economical approach to addressing this issue. These commercially proven technologies were selected as a means of reducing cooling pond acidity and eliminating the loss of water soluble P2O5 to the Gypsum Stack. The process provides improved recovery of phosphoric acid (water soluble P2O5) which directly results in improved Plant P2O5 efficiencies and lower P2O5 concentration in the cooling pond water. Phosphoric Acid is normally the highest concentration of the acidic components of the cooling pond water which must be neutralized prior to closure. Employing the Closed Loop Cooling Water System provides a P2O5 free transport fluid for stacking of phospho-gypsum which drastically reduces the loss of water soluble P2O5 to the gypsum stack. Alternatively process condensate from the closed loop circuit can be treated to recover the water for either reuse or discharge depending on the plant water balance. The combination of Series Filtration and Closed Loop Cooling along with an Acid Recovery System ultimately leads to a significant reduction in cooling pond water acidity and recovers the valuable constituents which would make the cooling ponds a financial liability at closure. Improved overall recovery of P2O5 can translate into an income of between $76 and $120 million over a 15 year period. Assuming a cost of $20/1000 gallons to lime neutralize cooling pond water for a 1.5 billion gallon cooling pond, would avoid over
$30 million in treatment costs. This brings the total financial benefit to $100 to $150 million over a 15 year period. There are significant paybacks for the implementation of these processes while a phosphoric acid plant is in operation.

Introduction

Phosphate producers normally utilize commingled cooling ponds and gypsum stacks to store acidic process water and by-product phospho-gypsum from wet process phosphoric acid production. The cooling pond water is utilized to remove the exothermic heat of reaction from the phosphoric acid plant reaction system, water vapors from the evaporation system and absorb fluorine from the phosphoric acid and granulation plants, and to transport the phospho-gypsum to the gypsum stack. Fundamentally, closed circuit utilization of the process water results in an accumulation of phosphoric acid, sulfuric acid and hydrofluorosilicic acid (FSA) in the cooling pond water. Over time, the concentration of these acids in the cooling pond water increase until they reach a point of equilibrium where the amount of these impurities lost to the free moisture in the gypsum stack equals the quantities of these acids that enter into the system. Currently increasingly stringent controls, particularly fluorides are being placed on the management of cooling ponds or cooling towers and gypsum stacking systems which places a considerable burden on producers as they try to compete in a global economy.

Hatch has evaluated the use of Series (Double) Filtration (where the phospho-gypsum is mixed with process water and re-filtered using counter current washing), Closed Loop Cooling utilizing heat exchangers between the existing process barometric condenser water streams and cooling pond/tower, Acid Recovery Systems and Phosphoric Acid Plant Cooling Water Treatment in order to achieve the following goals:

- Reduce the acidity of the pond water
- Increase overall Phosphoric Acid Plant P₂O₅ Recovery
- Reduce or eliminate acid handling losses to the cooling ponds
- Recover the acid constituents of the pond water as finished products
- Eliminate the loss of these valuable constituents to the gypsum stack
- Provide Fluoride free Cooling Tower/Pond operation.
- Provide quality water suitable for discharge or reuse.
**Fundamentals (Figures 1 & 2)**

The concentration of $P_{2}O_{5}$ in the cooling pond water is directly proportional to the loss of water soluble $P_{2}O_{5}$ from the phosphoric acid plant which means that in order to reduce the concentration of $P_{2}O_{5}$ in the cooling pond water, it is necessary to improve the recovery of $P_{2}O_{5}$. Phosphoric Acid Plant Filtration efficiency and Acid Handling Losses both contribute to the concentration of $P_{2}O_{5}$ in the cooling pond water.

- Typical Current Phosphoric Acid Plant Operation Water Soluble $P_{2}O_{5}$ Losses
  - Filtration Water Soluble $P_{2}O_{5}$ Loss – 2 to 6% of $P_{2}O_{5}$ Fed
  - Acid Handling Losses - 3 to 5% of $P_{2}O_{5}$ Fed

![Figure 1 - $P_{2}O_{5}$ Concentration as a Function of WS Losses](image)

Filtration theory tells us that the filtration rate and filter cake wash throughput rate are inversely proportional to the cake thickness assuming the cake is of uniform thickness. In practice however, the differential pressure across the filter is not uniform due to non-uniform filter cake thickness and areas within the cake that have higher filtration resistance due to scaling of the filter cloth and very low resistance due to holes in the cloth. The filter product acid and wash liquors will take the path of least resistance...
leaving the high resistance zones unwashed or washed to a lesser extent. This results in localized zones in the filter cake which have poor filtration and wash efficiencies leaving high quantities of water soluble P\textsubscript{2}O\textsubscript{5} in the gypsum cake.

**Series (Double) Filtration (Figure 3)**

Series Filtration is a commercially proven technology which consists of re-filtering the phospho-gypsum from the primary phosphoric acid plant filter on a second filter and washing the cake with process water prior to final discharge of the gypsum cake. The No. 1 filtrate from the second filter in series is used as the wash liquor on the primary or first filter in the series filtration process. The mixing of the phospho-gypsum cake from the first filter with the No. 2 filtrate recovered from the second filter to produce a slurry which releases the phosphoric acid that is trapped in the filter cake. The trapped P\textsubscript{2}O\textsubscript{5} is due to imperfects in the formation of the cake (varying resistance), the cake filterability and the washing efficiency of the phospho-gypsum. Filtering the phospho-gypsum cake a second time provides an opportunity to recover the trapped pockets of product phosphoric acid and any hydraulic loses from the primary filter. Another advantage of series filtration is that in combination with a closed loop Acid Recovery System, all phosphoric acid plant acid handling losses and wash losses can be sent to the second filter for recovery of the P\textsubscript{2}O\textsubscript{5}. Double filtration is also applicable to the Hemi-Di-hydrate Process where a portion of the wash water is consumed in the transformation of the Hemi-hydrate to stable Di-hydrate gypsum and the recovery of citrate soluble P\textsubscript{2}O\textsubscript{5} losses.

The improvement in P\textsubscript{2}O\textsubscript{5} efficiency from washing the phosphoric acid from the gypsum cake increases the overall recovery of P\textsubscript{2}O\textsubscript{5} and results in a lower equilibrium P\textsubscript{2}O\textsubscript{5} concentration in the cooling pond water. Throughout the transition to the new equilibrium concentration, P\textsubscript{2}O\textsubscript{5} is “harvested” from the cooling pond system and is converted into phosphoric acid product. When the equilibrium concentration is reached the plant continues to operate at the higher P\textsubscript{2}O\textsubscript{5} efficiency level. The removal of P\textsubscript{2}O\textsubscript{5} and subsequent lower equilibrium P\textsubscript{2}O\textsubscript{5} content of the cooling pond water reduces cooling pond acidity.

The Process Block Flow Diagram is shown in Figure 3.
Closed Loop Cooling System (Figure 4 & Table 1)

In the Closed Loop Cooling System the cooling function of the Cooling Pond is replaced by the installation of a Cooling Tower which removes heat from the Phosphoric Acid Plant process equipment. Since any fluoride entering into the cooling tower water would be stripped out by the air flow through the cooling tower and eventually end up in the atmosphere, the amount of fluoride entering the cooling tower water must be minimized. This can be accomplished by installing a heat exchanger between the Cooling Tower and the Barometric Condensers and Fume Scrubber water systems.

The heat exchangers remove heat from the water that is condensed in the barometric condensers and scrubbers as well as the fluoride vapors picked up by the cooling water. The fluorides are contained within the closed loop cooling water circuit. The amount of Fluorine entering the closed loop cooling water circuit can be minimized by installing FSA Recovery Systems upstream of the reactor and evaporator barometric condensers.
The Closed Loop Cooling System is shown in Figure 4. This Block Flow Diagram is based on concentrating enough P₂O₅ from a nominal 26% to 52% P₂O₅ to produce a 38% P₂O₅ feed to the DAP Plant.

The predicted chemical analysis of the closed loop water as compared to cooling pond water is as follows:

**TABLE 1 - Pond Water / Closed Loop Water Comparison**

<table>
<thead>
<tr>
<th>Component</th>
<th>Conventional Pond Water</th>
<th>Closed Loop Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>% P₂O₅</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>% F</td>
<td>1.3</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>% SO₄</td>
<td>0.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Integrated Series Filtration Closed Loop Phosphoric Acid Process (Figure 5)**

Overall 3.2 tons of water vapor enters the closed cooling water loop per ton of P₂O₅ produced. The condensed vapor has to be consumed in the process; otherwise it would accumulate very rapidly. The closed loop cooling water which contains low levels
of fluoride and little or no P₂O₅ is can be used as filter cake wash water on the secondary filter as shown in Figure 5.

**Figure 5 - Integrated Series Filtration / Closed Loop Cooling System**

In the above process, 4.1 tons of cake wash water per ton of P₂O₅ produced is required to wash the gypsum cake. The closed loop requires in excess of 3.2 tons of water to be removed per ton of P₂O₅ in order to maintain process inventory. This process requires approximately 0.9 tons of makeup water per ton of P₂O₅ to meet the demand of the gypsum filter and the process. The makeup water can be either cooling pond water or recovered plant wash water. The use of cooling pond water allows the existing cooling ponds to be reduced in P₂O₅ and for P₂O₅ to be recovered over a period of time. Closed Loop Water from the gypsum stack is also used to slurry the gypsum discharging the second filter for transport to the gypsum stack. The use of the P₂O₅ free water minimizes the loss of P₂O₅ to the gypsum stack.

**Reduction of Cooling Pond Acidity (Figure 6)**
The Series Filtration process provides for improved recovery of phosphoric acid (water soluble P$_2$O$_5$) which directly results in a lower P$_2$O$_5$ concentration in the cooling pond water. Employing the Closed Loop Cooling Water System provides a P$_2$O$_5$ free transport fluid for stacking of phospho-gypsum which significantly reduces the loss of water soluble P$_2$O$_5$ to the gypsum stack. As can be seen in Figure 6, the concentration of P$_2$O$_5$ in the cooling pond water is rapidly reduced during the first ten years of operation and then asymptotically approaches a new equilibrium. This rapid reduction in P$_2$O$_5$ concentration quickly reduces the acidity of the cooling pond water.

Figure 6 – Reduction in Cooling Pond Acidity
Resource Recovery

In a typical phosphoric acid plant, acid handling losses can easily exceed 3 to 5% of the P₂O₅ produced. During the manufacture of phosphoric acid there are a number of phosphate containing streams that can be misdirected, drained, leaked, or overflow from vessels during the production process. These streams can be collected and returned to the wet process phosphoric acid plant or the secondary filter to improve plant P₂O₅ recovery. The return of these streams typically includes closed loop wash systems, circulation pumps, acid collection tanks and sumps. These systems can provide a means to recover phosphate bearing solutions from process tank drainage and cleaning in addition to pipe line washing activities. These recovery systems can reduce the quantity of phosphate reporting to the gypsum stack or gypsum discharge stream and allow a reduction of the acidity of the comingled gypsum stack and cooling pond system.

Resource Recovery Systems need to be an integral part of the loss management system in order to recover water soluble P₂O₅ handling losses in order to reach the minimum P₂O₅ concentration in the cooling pond.

Figure 7 - Integrated Loss Management
Phosphoric Acid Plant Cooling Water Treatment

Hatch assembled a Global Team in order to collaborate on an alternative approach to treating Phosphoric Acid Plant Cooling Water. In a novel approach it was decided to treat the condensed vapors directly from the process rather than treat the cooling pond water with its inherent difficulties. The Concept is depicted in Figure 8 below.

Figure 8 - Integrated Series Filtration / Closed Loop Cooling System/ Water Treatment

- High recovery of fluorides at low concentration during vapor condensation
- Very little if any contaminants in condensed vapors
- Eliminates flow of fluorides to the cooling pond or tower
- Recovery of water is much higher than current pond water treatment processes
- Over 96% recovery of fluorides as commercial grade FSA suitable for sale or further processing
- Over 89% of water recovered as very low conductivity high quality water suitable for discharge or reuse as cooling tower makeup
The collaboration team included Process Engineers from the Tampa Office as well as Scientists and Test Facilities in Australia and Technology experts from Canada.

Figure 9 - Hatch Global Collaboration

A simplified Block Flow Diagram for the Treatment Process is shown in Figure 10. Since we are currently pursuing patent protection of the proprietary technology we are very limited as to what can be shared publically at this time.
The mass balance developed from the testing conducted in Australia is shown in Table 2. Results indicated that 89% of the water can be recovered and that 96% of the FSA was extracted with a concentration in excess of 15%. The test facility had limited capability but experience dictates that even higher recovery of water and higher concentrations of FSA are achievable.

Currently negotiations are under way with equipment suppliers to conduct pilot plant testing of the process to establish the upper limits of water recovery and FSA strength and recovery and provide sufficient design information to allow for reasonable capital cost estimates for a commercial facility. Plans are also underway to conduct in-plant testing on portion of the evaporation system to demonstrate the process and quantify impacts of upset conditions and provide a basis for designing counter measures to mitigate those impacts.
System Impact (Figure 12)

The overall improvement in P₂O₅ efficiency from washing the phosphoric acid from the gypsum cake and freeing up the trap phosphoric acid increases the recovery of P₂O₅ by 6.2% on average. During the transition to the new lower equilibrium concentration, additional P₂O₅ is removed from the cooling pond system and converted into finished product. After the equilibrium concentration is reached, the plant continues to operate at the higher efficiency level shown below. The final overall P₂O₅ Recovery is 96% comprised almost entirely of reaction losses (CI & CS P₂O₅).

As can be seen in Figure 12 the addition of the Cooling Water Treatment Process and subsequent ability to discharge quality water in excess of the amount required to displace pond water increases the rate of removal of P₂O₅ from the pond. The consumption of pond water is almost triple leading to the tripling of the recovery of P₂O₅ from the pond. This allows 80% of the P₂O₅ to be recovered from the pond in just 5 years.
Financial Benefit (Figure 13)

The financial benefit from the use of these process technologies is derived from three sources:

1. WS P₂O₅ in the existing cooling pond system is converted into finished products.
2. A higher overall recovery of P₂O₅ fed to the plant for the life of the plant.
3. The reduction in the acidity of the cooling pond leads to a significant reduction in the cost of treatment at the plant closure.

Example Basis (existing plant):

- 550,000 stpy P₂O₅ Production Capacity
- 5.0% WS P₂O₅ Loss
- Cooling Pond:
  - Volume: 1.5 billion gallons
  - Equilibrium P₂O₅ Concentration: 2.0 wt%
A 1.5 billion gallon Cooling Pond with a 2.0% P₂O₅ concentration contains approximately 130,000 tons of P₂O₅. At an avoided raw material cost of $150.00 per ton the recovery of the nutrient is valued at $19.5 million. Assuming a $250 per ton P₂O₅ margin the value increases to $32.5 million. Approximately 70 to 75% of the P₂O₅ value is recovered in seven years.

The plant P₂O₅ recovery efficiency is increased by 5.0% which represents approximately 25,000 tons of increased P₂O₅ production annually. At the $150 and $250 per ton P₂O₅ values, the annual revenue from increase P₂O₅ production is $3.75 and $6.25 million respectively. As can be seen in Figure 9 the annual revenues are quite high initially and falls off as the P₂O₅ in the cooling pond is recovered and levels out at the new plant efficiency for the remaining life of the facility. Overall between $55 and $95 million in income can be achieved over a 10 year period.

The third component of the final benefit is the savings in avoided operating expense associated with the lime neutralization of the cooling pond water at the closure of the facility. Assuming a cost of $20/1000 gallons to treat the cooling pond water for the plant in this example would avoid over $30 million in treatment costs. This brings the
total financial benefit over a 15 year life of plant period to between $85 and $125 million.

Equipment Considerations

Series Filtration

Early indications are that half of filter area is required to filter the gypsum on the second filter. Belt filters are being used in this application today. Existing gypsum tanks can be used to slurry the gypsum discharging from the primary filters. New pumps would be required to feed the second filter and new gypsum slurry tanks and agitators are need for the second stage filters. Existing gypsum transfer pumps could be used to transfer gypsum slurry from the second filter to the gypsum stack.

Closed Loop Cooling System

The existing pond water supply and return system could be used to provide closed loop water to condensers, scrubbers and for the final sluicing of gypsum. Plate and frame heat exchangers arrangements can be utilized for process cooling with the addition of a Process Condensate Circulating Tank and Circulating Pumps.

Resource Recovery

Resource Recovery Systems typically include closed loop wash systems, circulation pumps, acid collection tanks and sumps. These systems can provide a means to recover phosphate bearing solutions from process tank drainage and cleaning in addition to pipe line washing activities.

Conclusions

The addition of the Cooling Water Treatment Process can increase the recovery of P$_2$O$_5$ from the pond by almost three fold and significantly shorten the time table to remediate the cooling pond.

Preliminary test results are encouraging with over 96 % recovery of fluorides and 89% recovery of water.

However, more test work is required:

- Pilot Plant Testing is planned to validate Preliminary Test results for the recovery of fluoride and Water
- Partial Plant Demonstration Testing is needed to obtain real world results
Process aim is to dramatically reduce fluorides entering the cooling water circuits

Recovery of water is much higher than current pond water treatment processes

Improve plant water balance by providing high quality water for discharge thereby increasing the pond water demand for filter cake wash or makeup to cooling towers

References:

Bouffard, L., and Doug Belle 2014, “Phosphoric Acid Plant Sustainability”, CRU Phosphates 2014, Paris France


