MONEY IN THE BANK

A PROCESS FOR THE REDUCTION OF COOLING POND ACIDITY EMPLOYING SERIES FILTRATION OF PHOSPHO-GYPSUM COMBINED WITH THE ELIMINATION OF WATER SOLUBLE P_2O_5 LOSSES TO THE GYPSUM STACK USING THE CLOSED LOOP COOLING WATER CONCEPT.

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Abstract

As concerns over the financial liability associated with the final closure of a Phosphate Fertilizer Facility and the ultimate disposition of the cooling pond continues Central Engineering is evaluating the use of Series Filtration (Double Filtration) of phospho-gypsum and Closed Loop Cooling Water System as a more economical approach to addressing the issue. These commercially proven technologies were selected as a means of reducing the cooling ponds acidity and eliminating the loss of water soluble P_2O_5 to the Gypsum Stack. The process provides for an improved recovery of phosphoric acid (water soluble P_2O_5) which directly results in a lower P_2O_5 concentration in the cooling pond water. Phosphoric Acid is usually the highest concentration of the acidic component of the cooling water which must be neutralized prior to closure. The improved recovery of P_2O_5 also leads to improved recovery of sulfuric acid and ammonia as well. Employing the Closed Loop Cooling Water System provides a P_2O_5 free transport fluid for stacking of phospho-gypsum which drastically reduces the loss of water soluble P_2O_5 to the gypsum stack. This combination ultimately leads to the elimination of the cooling pond and recovers the valuable constituents which would make the cooling ponds a financial liability at closure. Improved overall recovery of P_2O_5 will translate as an income into between $44 and $74 million over a 10 year period. Assuming a cost of $20/1000 gallons to lime

neutralize the cooling pond water for the plant in this example, would avoid over $25 million in treatment costs. This brings the total financial benefit to $70 to $100 million over a 10 year period.

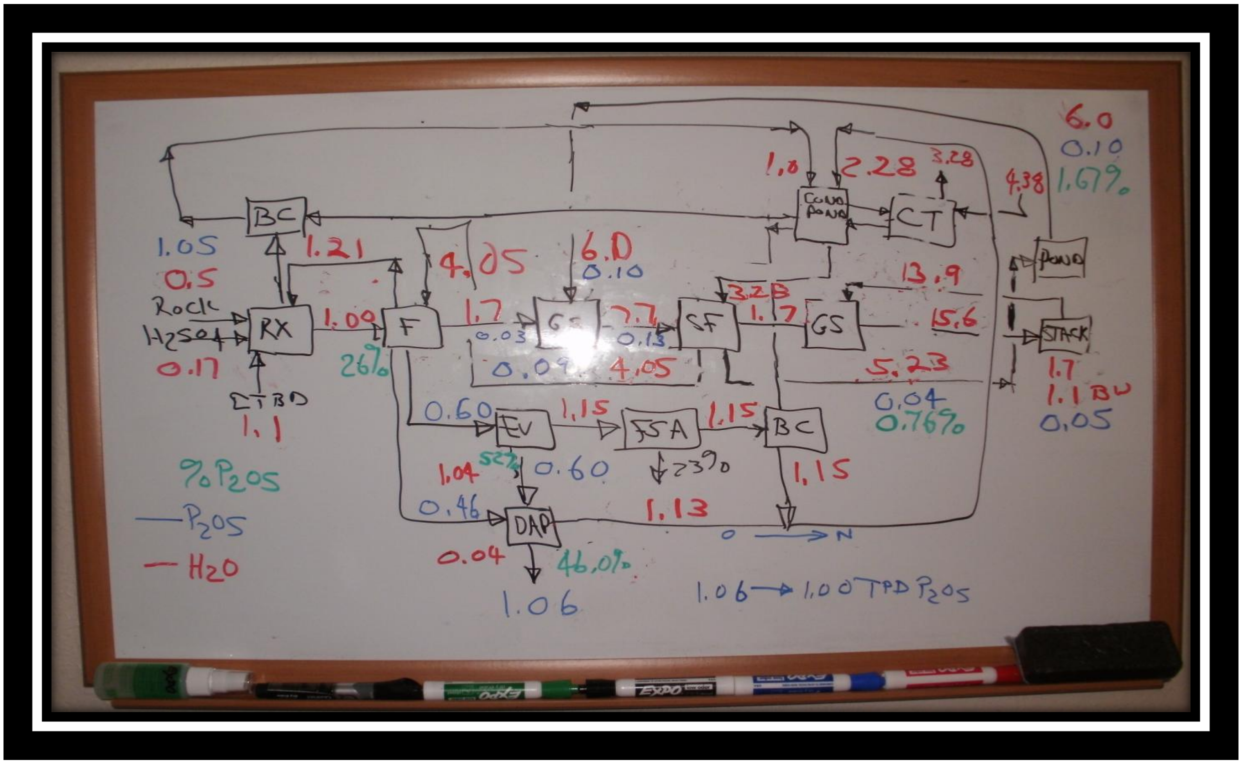
Introduction

Through the years phosphate producers have utilized a commingled cooling ponds and gypsum stacks to store acidic process water and by-product phospho-gypsum from the wet process phosphoric acid plant. The process water is used to remove the exothermic heats of reaction from the phosphoric acid plants, 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 in the process water until the concentration is high enough that the amounts lost to the gypsum stack as interstitial moisture is equal to the quantities of these constituents entering into the system. More and more stringent controls have been placed on the managers of these systems and this trend is continuing which is placing a considerable burden on the industry as it tries to compete in a global economy.

Central Engineering is evaluating the use of Series (Double) Filtration (where the phospho-gypsum is mixed with pond water and filtered using a counter current wash) along with Closed Loop Cooling employing water interchangers between the existing barometric condensers and the cooling tower achieves the following goals:

- Reduce the acidity of the pond water
- Reduce or eliminate 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

Not long after I started looking at the problem of what to do with Cooling Ponds a non-engineer fairly new to the engineering world came into my office and asked the age old question. “What does a Process Engineer do?” Well I pointed to my white board which I was using to develop a process sketch of the Series Filtration/ Closed Loop Cooling Concept and remarked that’s one thing a Process Engineer does. Process Engineers take existing process steps and puts them together to form an improved process resulting in a beneficial outcome.



Fundamentals

One of the basic principals in Chemical Engineering Calculations with respect to material balances is that:

Accumulation = Input minus output.

By definition, at equilibrium there is no longer an accumulation term. When the concentration of P_2O_5 in the pond water increases until the quantity of P_2O_5 in the moisture retained by the gypsum is equal to the losses from the manufacturing process the plant has reached equilibrium.

Therefore:

Input = Output, where output is the sum of Fertilizer Products and losses to the gypsum stack.

What this means is that the concentration of P_2O_5 in the pond water is directly proportional to the loss of water soluble P_2O_5 which in turns means that in order to reduce the concentration of P_2O_5 it is necessary to improve the recovery of P_2O_5. Filtration efficiency and material handling losses both contribute to the pond water concentration.

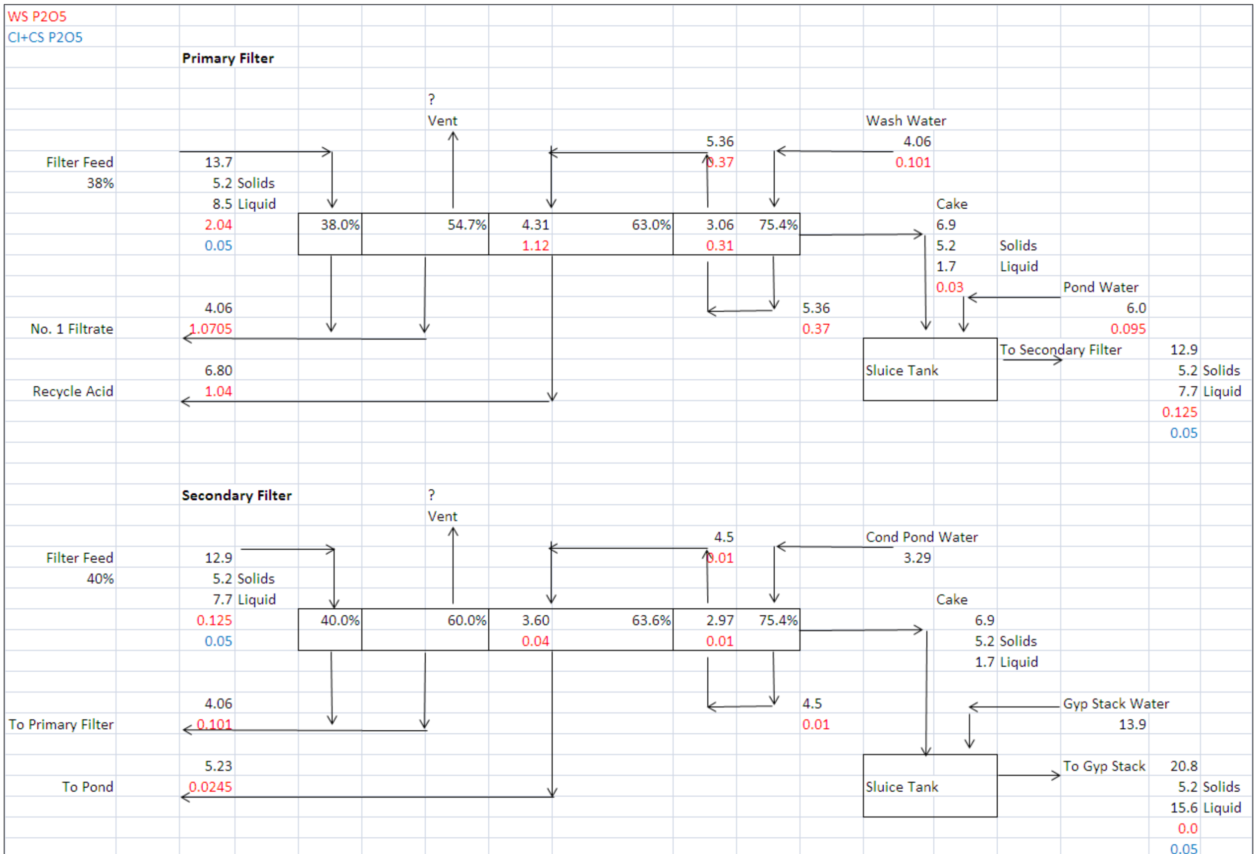
Filtration theory tells us that the filtration rate and wash throughput rate are inversely proportional to the cake thickness assuming the cake is of uniform thickness. In practice however the differential pressure across the filter is not uniform due to cakes which are not uniform in thickness and have areas of high resistance due to scaling of the filter cloth and low resistance areas due to holes in the cloth. The product acid and wash liquors tend to take the path of least resistance leaving the high resistance zones unwashed or washed to a lesser extent. This results in localized zones which have poor filtration and wash efficiencies leaving high quantities of water soluble P_2O_5 in the gypsum cake.

Series (Double) Filtration (Figure 1)

Series Filtration is a commercially proven technology which consists of filtering the phospho-gypsum from a phosphoric acid plant on a second filter and washing the cake with condensate pond water prior to disposing of the gypsum cake. The wash filtrate from the second or last 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 with cooling pond water to produce a slurry provides for the release of the trapped liquid containing various degrees of phosphoric acid. The trapped product results from the imperfection surrounding the formation of the cake (varying resistance), its filtration and the subsequent washing of the phospho-gypsum. Filtering the phosphor-gypsum cake a second time provides an opportunity to recover the trapped pockets of product phosphoric acid and any hydraulic looses from the primary filter. Another advantage of series filtration is that in combination with a closed loop plant wash system all handling losses and wash losses can be sent to the second filter for recovery of the $P_2O_{5.}$

The improvement from the efficiency of washing the phosphoric acid from the cake provides for an increase in the overall recovery of P_2O_5 and results in a lower equilibrium P_2O_5 concentration of the cooling pond water. Throughout the transition to the new equilibrium concentration, P_2O_5 is “harvested” from the cooling pond system similar to recovering phosphate rock form old phosphate mines and subsequently converted into a finished product. After the equilibrium concentration is reached the plant continues to operate at the higher efficiency level. The removal of P_2O_5 and subsequent lower equilibrium P_2O_5 content of the cooling pond water reduces its acidity. The Process Block Flow Diagram is shown below in Figure 1.

Figure 1- Series (Double) Filtration



Primary Filter Balance

In	Total	Solids	Liquid	WS P2O5	CI & CS P2O5
Filter Feed	13.7	5.2	8.5	2.21	0.05
Wash Water	4.06		4.03	0.09	
Pond Water	6		6	0.095	
	23.76	5.2	18.53	2.395	0.05
Out					
FS Filter Feed	12.9	5.2	7.7	0.125	0.05
Product Acid	4.06		4.08	1.06	
Recycle Acid	6.77		6.75	1.21	
Total	23.73	5.2	18.53	2.395	0.05

Secondary Filter Balance

In	Total	Solids	Liquid	WS P2O5	CI & CS P2O5
FS Filter Feed	12.9	5.2	7.7	0.125	0.05
Cond Pond Water	3.29		3.26		
Gyp Stack Water	13.9		13.9		
	30.09	5.2	24.86	0.125	0.05
Out					
Gyp Slurry	20.8	5.2	15.6		0.05
Product Acid	4.06		4.03	0.083	
Return Pond Wate	5.23		5.23	0.042	
Total	30.09	5.2	24.86	0.125	0.05

Closed Loop Cooling System (Figure 2 & 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 the heat from the Phosphoric Acid/ Granular Fertilizer facilities. Since any fluoride entering into the cooling tower water would be stripped out by the air flow and eventually end up in the atmosphere, no fluorine can be allowed into the cooling tower. This is done by inserting a Water Interchanger between the Cooling Tower and the Barometric Condensers and Fume Scrubbers in the plants.

Having installed the Heat Exchangers the water condensed in the barometric condensers and scrubbers as well as the fluoride vapor picked up by the cooling water is then contained within the closed loop. A system has to be devised to consume the condensed vapors as well as the handling of the fluoride compounds contained in the closed loop. The amount of Fluorine entering the closed loop is kept to a minimum by recovering it using conventional FSA Recovery Systems before the vapors are condensed. A simplified overall Phosphoric Acid /Granulation Plant water balance is given in Table 1.

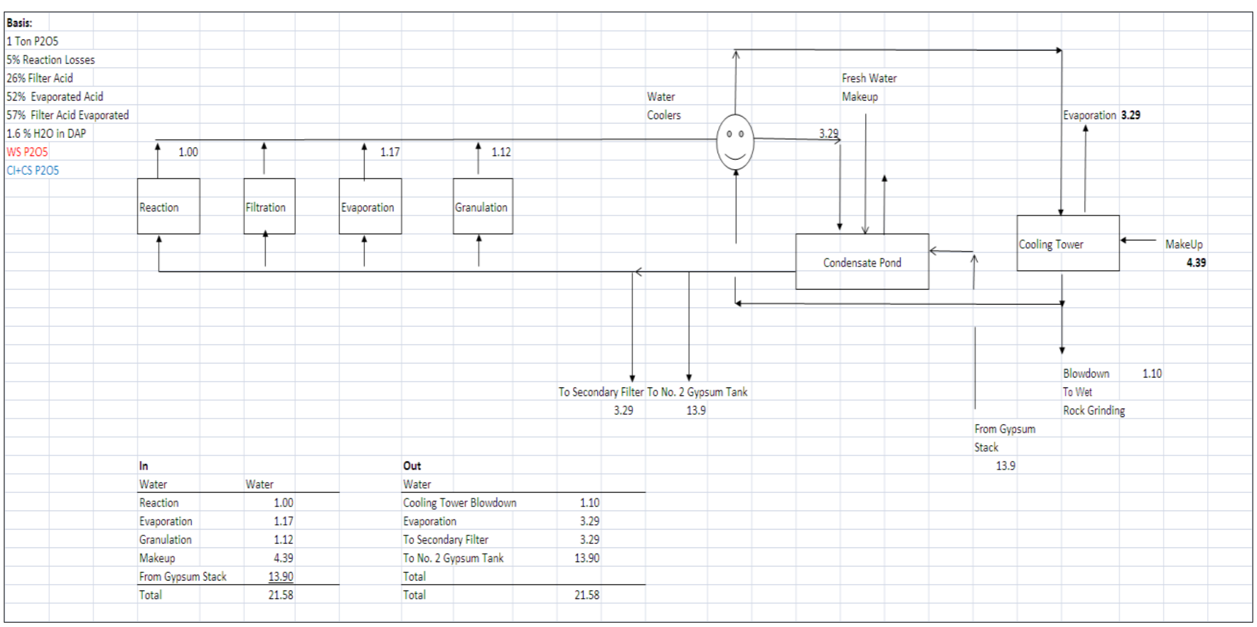
TABLE 1 - OVERALL WATER BALANCE

Basis: 1.0 Ton P_2O_5 Produced.

		Input Tons	Output Tons
Rock Slurry		1.60	
H2SO4	Free	0.06	
	Bonded	0.50	
DAP	Free		0.04
`	Bonded		0.09
Gypsum	Free		1.70
	Bonded		1.10
Makeup Water(By Difference)		0.77	
Total		2.93	2.93

The flow of water entering the closed loop is provided in Figure 2. This Block Flow Diagram is based on concentrating enough P_2O_5 from a nominal 26% to 52% P_2O_5 to produce a 38% P_2O_5 feed to the DAP Plant.

FIGURE 2 - CLOSED LOOP COOLING SYSTEM



Integrated Series Filtration Closed Loop Phosphoric Acid Process (Figure 3 & Table 2)

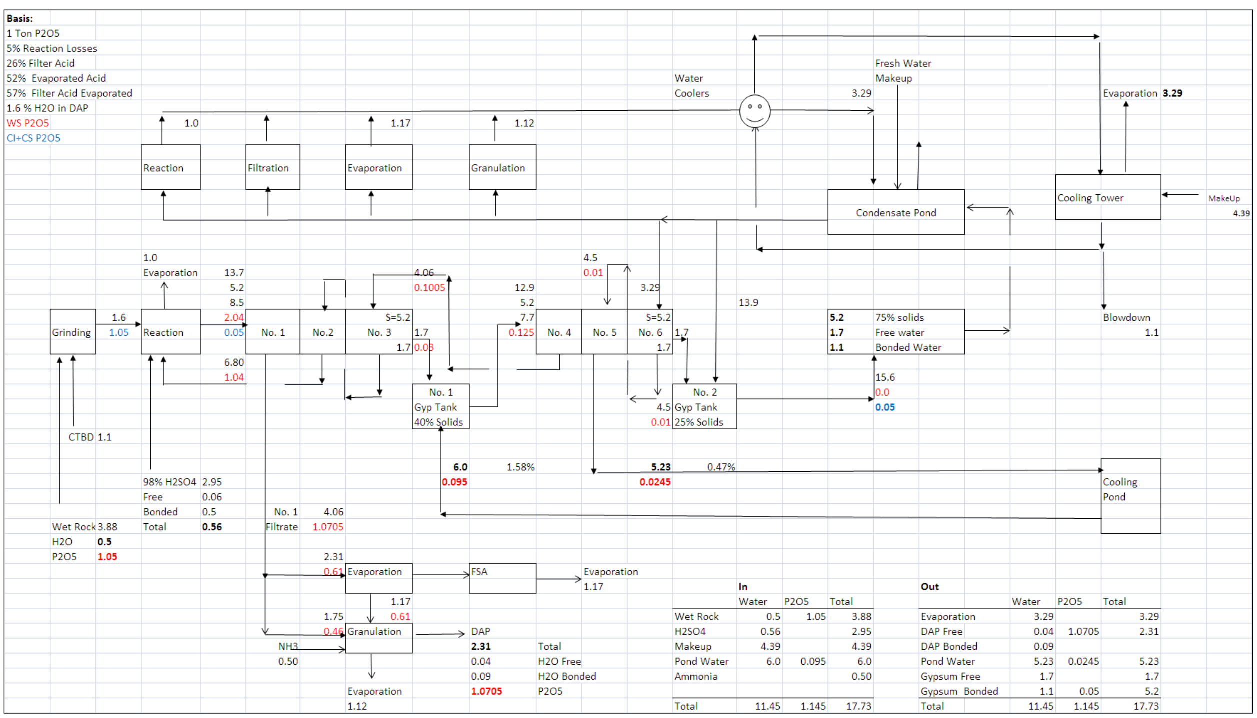
Overall 3.29 tons of water enters the closed loop per ton of P_2O_5 produced. The condensed vapor has to be consumed in the process; otherwise it would accumulate very rapidly. Fortunately there is a need for water containing very low amounts of fluorine and P_2O_5 in the Series Filtration Process as shown in Figure 3.

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

TABLE 2 - POND WATER/CLOSED LOOP WATER COMPARISON

Component	Conventional Pond Water	Closed Loop Water
% P_2O_5	1.58	0.00
% F	1.10	0.60
% SO_4	0.70	0.00
% NH_3	0.20	0.00

FIGURE 3 - INTEGRATED SERIES FILTRATION/ CLOSED LOOP COOLING SYSTEM



In	Water	P2O5	Total
Wet Rock	0.5	1.05	3.88
H2SO4	0.56		2.95
Makeup	4.39		4.39
Pond Water	6.0	0.095	6.0
Ammonia			0.50
Total	11.45	1.145	17.73

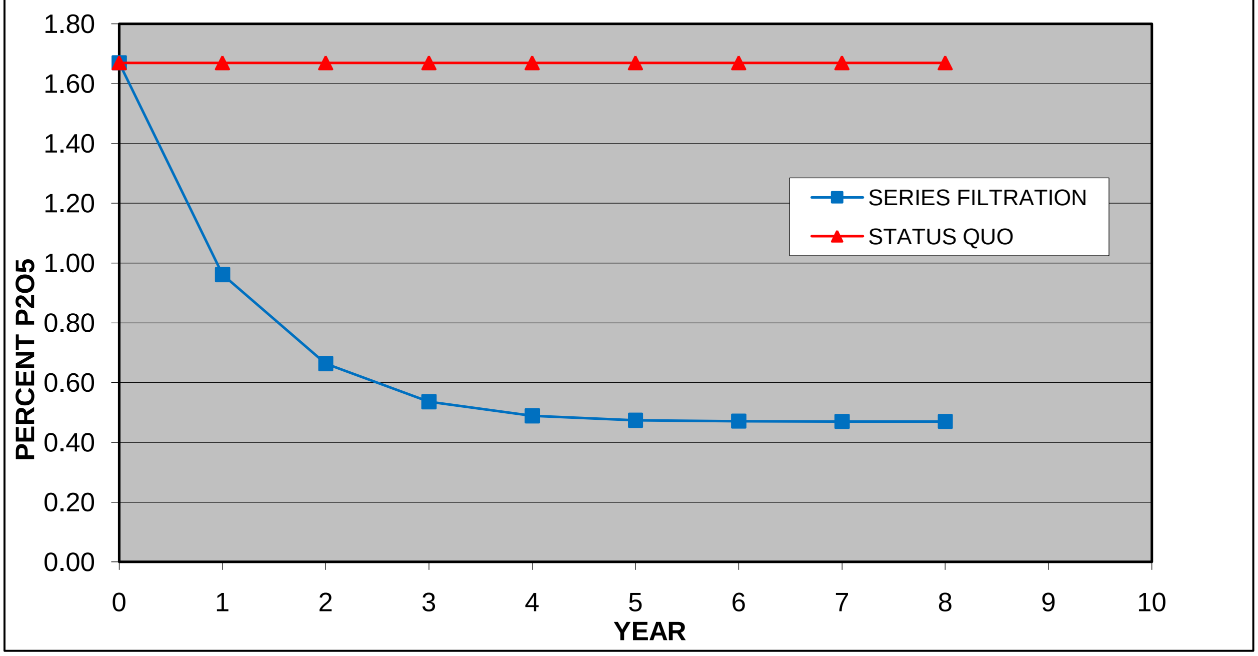
Out	Water	P2O5	Total
Evaporation	3.29		3.29
DAP Free	0.04	1.0705	2.31
DAP Bonded	0.09		
Pond Water	5.23	0.0245	5.23
Gypsum Free	1.7		1.7
Gypsum Bonded	1.1	0.05	5.2
Total	11.45	1.145	17.73

Normally 4 tons of wash water per ton of P_2O_5 produced is required to wash the gypsum cake. The closed loop requires in excess of 3 tons of water to be removed per ton of P_2O_5 in order to maintain process inventory. Therefore something less than 1 ton of makeup water per ton of P_2O_5 is required to meet both the demands of the gypsum filter and the process. The makeup water can be either cooling pond or fresh water. Cooling Pond water allows the existing cooling ponds to be reduced in volume and the P_2O_5, SO_4 and NH_3 to be recovered over a period of time. Once the cooling pond is eliminated fresh or rain water would be used to make up the water deficit. Closed Loop Water is also used to slurry the gypsum discharging the second filter for transport to the gypsum stack. The use of the P_2O_5 free water eliminates the stacking loss of P_2O_5 and is decanted from the gypsum and subsequently returned to the close loop.

Reduction and Elimination of Cooling Pond Acidity and Volume (Figure 4 & 5)

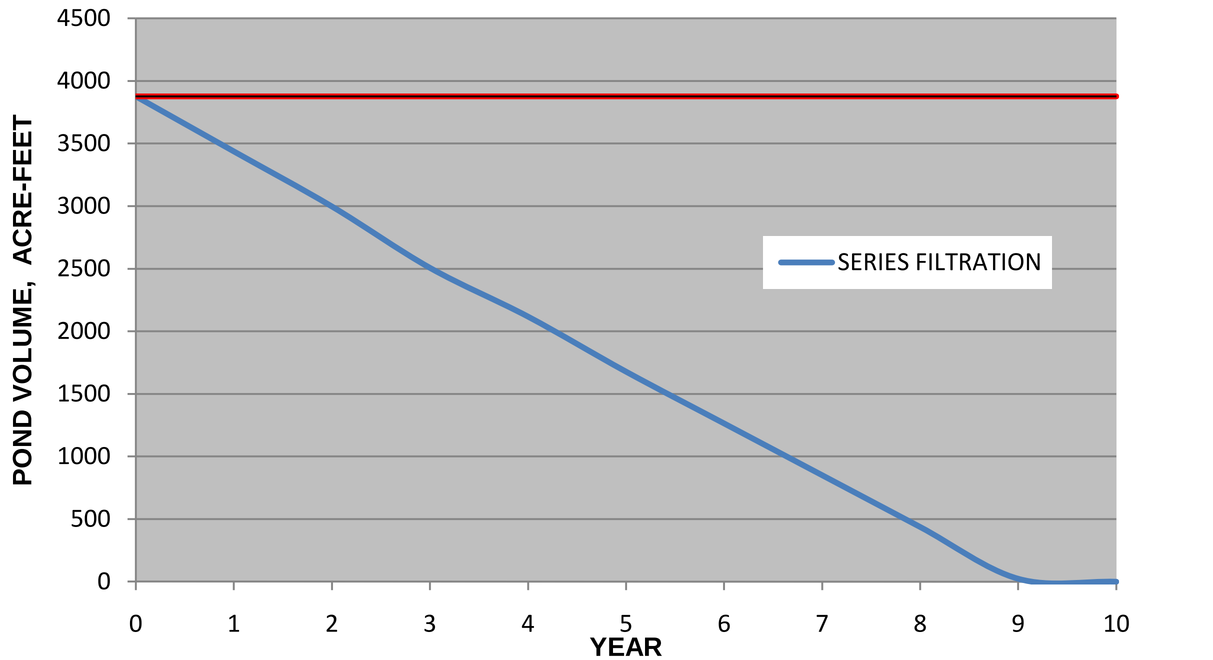
The process provides for an improved recovery of phosphoric acid (water soluble P_2O_5) which directly results in a lower P_2O_5 concentration in the cooling pond water. The improved recovery of P_2O_5 also leads to improved recovery of sulfuric acid and ammonia as well. Employing the Closed Loop Cooling Water System provides a P_2O_5 free transport fluid for stacking of phospho-gypsum which drastically reduces the loss of water soluble P_2O_5 to the gypsum stack. This combination ultimately leads to the elimination of the Cooling Pond and recovers the valuable constituents. As can be seen in Figure 4, the concentration of P_2O_5 reduces dramatically the first three years and then asymptotically approaches a new equilibrium.

FIGURE 4 - POND WATER P_2O_5 CONCENTRATION



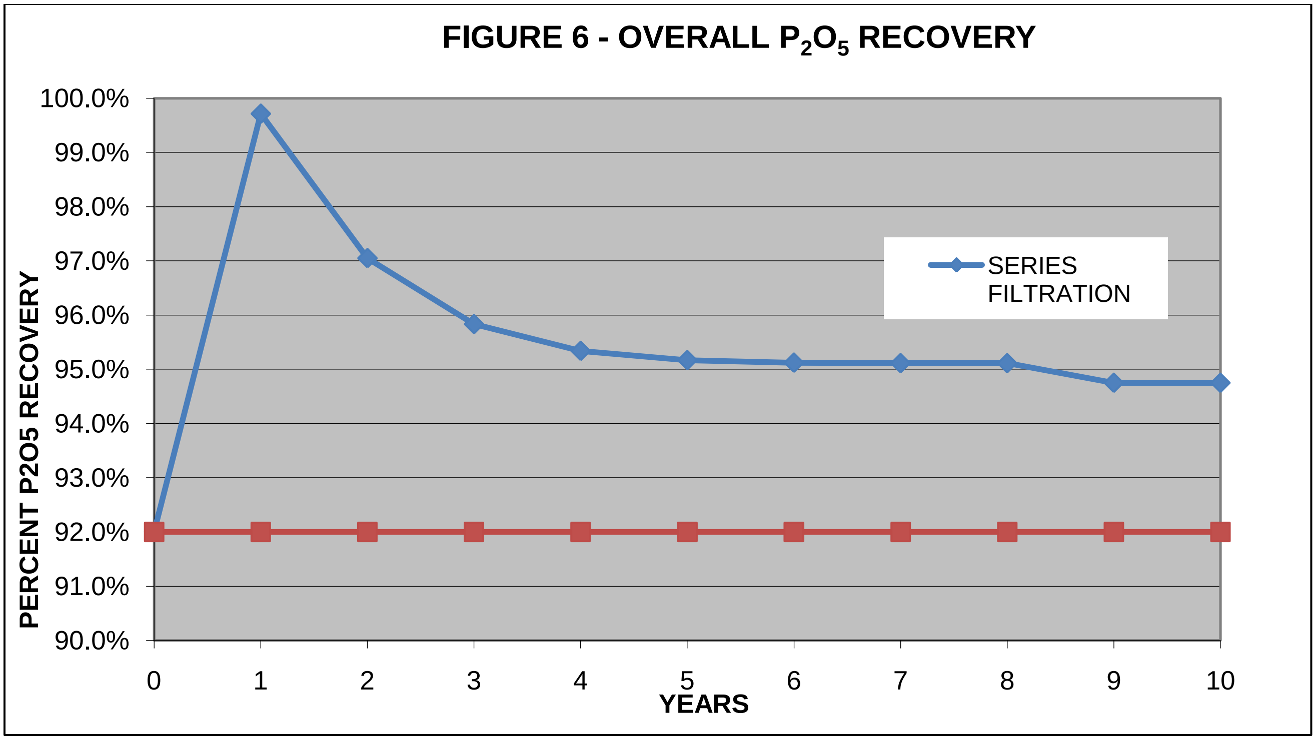
This rapid reduction in concentration would quickly demonstrate significant progress in reducing the acidity of the cooling pond. Towards the end of Year 8 the volume of the pond is reduced to zero as can be seen in Figure 5 below.

FIGURE 5 - COOLING POND VOLUME REDUCTION



System Impact (Figure 6)

The improvement from the efficiency of washing the phosphoric acid from the gypsum cake freeing up the trap phosphoric acid provides for an increase in the recovery of P_2O_5 of 2.75% as illustrated in Figure 6. During the transition to the new lower equilibrium concentration, additional P_2O_5 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 Overall P_2O_5 Recovery is 95% comprised almost entirely of reaction losses (CI &CS P_2O_5).



Financial Benefit (Figure 7 & Table 3)

The financial benefit from the use of the Technologies is derived from three sources:

1. The removal of WS P_2O_5 from the existing cooling pond system is converted into finished products.
2. A higher overall recovery of P_2O_5 fed to the plant for the life of the plant.
3. The reduction in the acidity of the cooling pond and the elimination of the cooling pond which leads to a significant reduction in the cost of treatment at the plant closure.

Example Basis (existing plant):

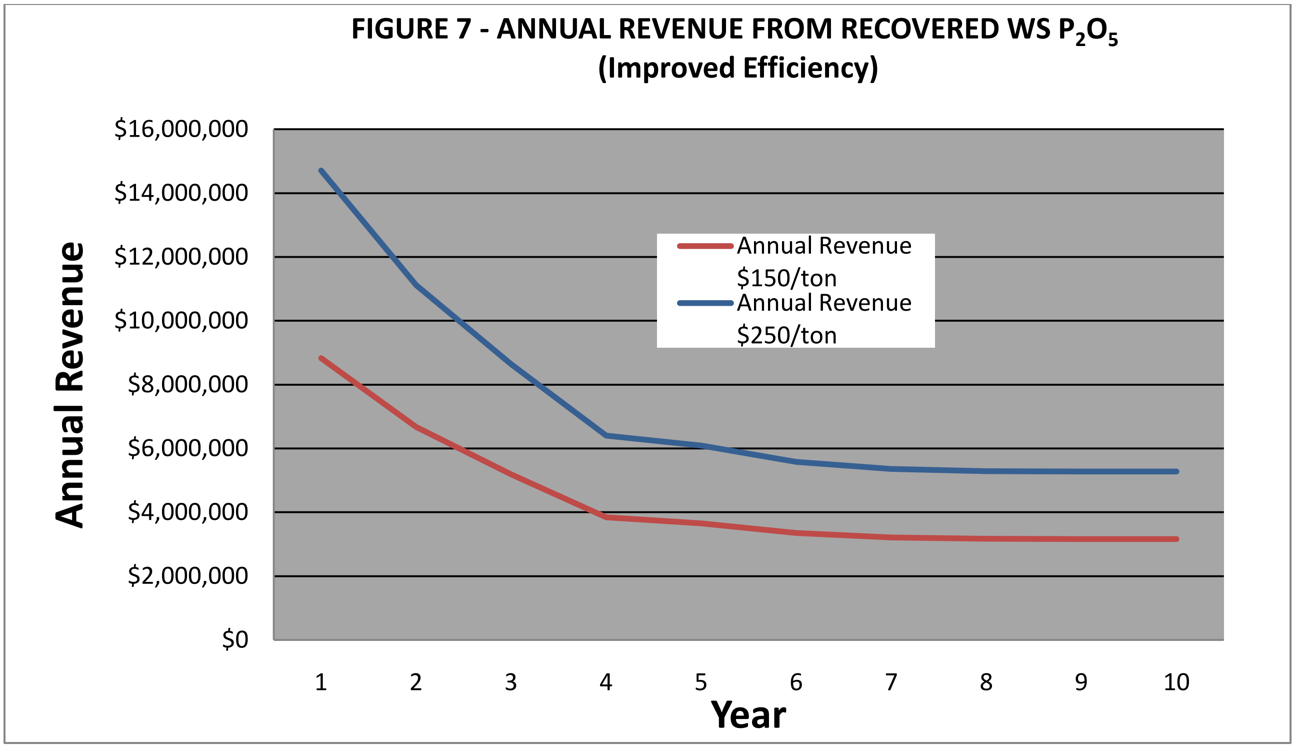
- 2000 TPD P_2O_5 Production Capacity
- 2.75% WS P_2O_5 Loss
- Cooling Pond :
  - Size; 3800 Acre-Feet (325,581 gals/ ac-ft)
  - Equilibrium P_2O_5 Concentration; 1.58 %

A 3800 Acre-Foot Cooling Pond with a 1.58% P_2O_5 concentration contains over 82,500 tons of P_2O_5. At an avoided raw material cost of $150.00 per ton the recovery of the nutrient is valued at $12million. Assuming a $250 per ton P_2O_5 margin the value increases to $21 million. In either case almost 90% of the value is recovered in three years.

The recovery of P_2O_5 from the process is reduced by 2.75 % which represents approximately 21,000 tons of P_2O_5. At the $150 and $250 values as shown below in Table 3 the annual revenue is $3.15 and 5.25 million respectively. As can be seen in Figure 7 the annual revenues are quite high initially and falls off as the P_2O_5 in the cooling pond is recovered and levels out at the new Plant efficiency for the life of the facility. Overall between $44 and $74million in income can be made over a 10 year period. These figures do not include additional income derived from the recovery of the sulfuric acid and ammonia components of the cooling pond water.

TABLE 3 - COMMULATIVE ANNUAL REVENUES

Year	Annual Production Tons	Recovered Tons P_2O_5	Overall Annual Revenue $150/ton	Harvested P_2O_5 Annual Revenue $150/ton	Overall Annual Revenue $250/ton	Harvested P_2O_5 Annual Revenue $250/ton
0	706979	0	0	0	0	0
1	765829	58850	8827500	5663400	14712500	9439000
2	751436	44457	6668550	3504450	11114250	5840750
3	741552	34573	5185950	2021850	8643250	3369750
4	732598	25619	3842796	678696	6404660	1131160
5	731333	24354	3653100	489000	6088500	815000
6	729302	22323	3348450	184350	5580750	307250
7	728405	21426	3213900	49800	5356500	83000
8	728119	21140	3171000	6900	5285000	11500
9	728074	21095	3164250	150	5273750	250
10	728073	21094	3164100	0	5273500	0
Year	Total	294931	44,239,596	12,598,596	73,732,660	20997660
Total including avoided neutralization cost			69,004,303		98,497,367	



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 $25 million in treatment costs. This brings the total financial benefit to $70 to $100 million.

Equipment Considerations

Series Filtration

Early indications are that 10 ton P_2O_5/m^2 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 could be used to slurry the gypsum discharging 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 disposal pumps could be used to transfer gypsum slurry from the second filter to the gypsum stack. Preliminary assessments are that Series Filtration should payout in less than one year.

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 heat exchangers arrangements similar to the Pond Water Heat Input Systems currently in service will be provided along with Cooling Towers and Circulating Pumps.

Conclusions

Commercially proven technologies exist that could be used to reduce the acidity and volume of Pond Water Cooling Ponds and recover the acids in the pond water and increase the overall efficiency of the Phosphate Fertilizer Plant. Coupled with the savings for the avoided cost of treatment at closure could provide between $70 and $100 million. The reduction in acidity is fairly rapid and within a few years this change would demonstrate very clearly that the financial liability associated with Pond Water Cooling Ponds was being mitigated. This is a win-win situation for the Industry and the Public in general.

"There is no better time or better economics to eliminate cooling ponds and recover P_2O_5 from ponds than while the plant is in operation!" John L. Martinez P.E., Fellow AIChE

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