INTRODUCTION

The management of process water is a key issue for the phosphate industry. The environmental liability and potential costs associated with the treatment of process water for discharge have the potential to add millions of dollars to operating cost. In addition, the conventional two stage neutralization with lime does not typically meet water discharge standards. Nitrogen, phosphorus, and fluoride levels can be achieved but the conductivity standard cannot. Most plants require a zone of discharge or water to blend with the neutralized water in order to meet the conductivity standard.

Process water systems in today's phosphate chemical plants typically circulate 50,000 to 150,000 gallons per minute of water for a variety of uses. The water in these systems is supplied from collected rainwater and well water. This water is reused extensively in the chemical plants for such purposes as fume scrubbing, filter washing, transport of gypsum, and direct contact cooling. Because of its direct contact with the process the water contains dilute phosphoric acid, sulfuric acid, fluosilicic acid, nitrogen, and sodium in addition to a variety of associated impurities.

Process water inventories which include cooling ponds and gypsum stack pore water commonly are in the billions of gallons. Impurities in this water constitute a double edged sword. On the one hand, they give the water an acidic nature which makes the water an environmental liability. On the other hand, the impurities represent economic potential in the form of recovered raw materials or alternative products. Because of the extensive inventory of water retained in cooling ponds and gypsum stack pore volume, this water represents millions of dollars in accumulated treatment or raw material costs.

To minimize these costs, companies have implemented water management plans which reduce both freshwater and waste inputs to the process water system, and which reduce rainshed collection areas.

Recently, the issue of gypsum stack closure has focused the industry on process water management. As existing stacks are closed, the stacks cease acting like giant "sponges" and seepage from the closed stacks must be incorporated into the process water balance as a new input. With the added liabilities created by waste discharges to the system and financial responsibility issues of closure, companies have been seeking new ways to manage process water systems.

At CF Industries Plant City Phosphate Complex a program of process water management has been evolving over a period of years. This plan has addressed the following concepts: (1) prevention of surface and groundwater contamination, (2) minimizing contamination of process water, (3) water balances and inventory measurements, (4) water reuse, and (5) gypsum stack closure. This paper presents some of the background of a management plan which is thought to be typical of the phosphate industry.

CONTAMINATION PREVENTION

An important factor in modern process water management is the consideration of pollution prevention and compliance with environmental and resource conservation laws and rules. No industrial or commercial facility can be allowed to continue operating indefinitely with practices that cause pollution of the environment or threats to public health or employee health.

The water management practices of the CFI Plant City Complex are regulated by a number of government agencies, including the United States Environmental Protection Agency, the Florida Department of Environmental Protection, the Hillsborough County Environmental Protection Commission, and the Southwest Florida Water Management District. The regulations to which the plant is subject are authorized by the Federal Water Pollution Control Act, the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Safe Drinking Water Act, and various state and county laws and ordinances.

The prevention of surface and groundwater contamination by process water has been a primary focus at the CFI Complex since the mid-70's.

Surface Water Contamination

Process water is a mixture of dilute phosphoric, fluosilicic, and sulfuric acids containing numerous dissolved cations originating from the phosphate rock and ammonia raw materials used in the manufacturing processes. The pH of the water ranges from 1.4 to 2.0. All the environmentally-objectionable constituents of the water are inorganic. Due to the low pH characteristics, the water qualifies as a hazardous waste under RCRA, but was exempted from hazardous waste regulations because the degree of hazard is low and treatment of the water is prohibitively expensive. Prior to 1975, the surface water discharge of treated process water as authorized by the NPDES and Florida Industrial Wastewater Discharge permits was a common practice. By means of water conservation and freshwater reuse projects, process water discharge was terminated in 1975 and combined non-process water and stormwater discharge has been reduced from 1 million gallons per day prior to 1988, to an average of 0.13 mgd. At the same time, the quality of the discharge has been greatly improved by the use of water quality monitoring, diversion systems, and vegetative nutrient consumption ponds (artificial wetlands). Compliance with ever-tightening surface water permit limits, including bioassay testing, has not been a problem.

Groundwater Contamination

Groundwater contamination, on the other hand, has been discovered and addressed in a 1987 consent order with the Florida DEP. The DEP rules allow a zone of discharge, for existing facilities, to the facility property boundary existing as of 1983. The 1983 boundary at the CFI Complex was within 150 feet. of the edge of the cooling pond. A pond over-topping incident in 1968 and seepage from a portion of the original 1964 cooling pond structure, resulted in groundwater contamination outside the zone of discharge at the south property boundary. The contamination assessment study triggered by this violation revealed, not surprisingly, seepage from the existing unlined system extending as far as three hundred feet from the edge of the system at various locations around the entire perimeter.

In order to address this groundwater release, CFI developed a plan to transfer all its operations to lined systems and to cap and drain the existing unlined system. CFI management, in consideration of local government plans for a public water supply wellfield to be located adjacent to the facility property determined to provide an extra layer of protective liner beyond the requirements of Florida rules, and to expedite the implementation of the plan.

To remediate the existing groundwater contamination, the consent order remedial action plan proposed the installation of six groundwater recovery wells which will collect the groundwater and transfer it to the water supply system of the complex. These wells will be installed during 1996 upon completion of permitting. The water produced will replace equivalent existing groundwater withdrawals from two deeper supply wells.

Progress to date on the lining plan has been significant. A lined, 80-acre process water cooling pond with a thirteen-acre emergency overflow containment was completed in August, 1995, at a cost of $15MM. The liner was the rule-design inverted composite liner laid on top of a six-inch compacted clay base. The clay permeability specification was 10^{-7} cm./sec. The inverted composite liner was a sixty-mil HDPE plastic geomembrane liner covered with 24 inches of gypsum compacted to 10^{-4} cm./sec. permeability. The liner system is illustrated in Figure 1.

Also completed in 1995 was the last of a series of projects totaling over $2.5MM to line and pave all areas of the complex that were subject to potential leaks or spills of chemicals. These areas, primarily located beneath pipe racks and surrounding tanks, were first lined with 60-mil HDPE geomembrane and then paved with concrete or asphalt. The paving was sloped and ditched to collect any spills and transfer them to the process water system.

The final, and largest, lining project is a 522-acre gypsum storage area immediately south of the existing storage system. The land for this system was acquired from Hillsborough County ownership in September 1995. Land use approvals and permitting are currently being processed as a demonstration project under Florida's new Ecosystem Management Act. The liner proposed for this area consists of two 60-mil HDPE geomembranes separated by 24 inches of compacted gypsum. The gypsum stack expansion liner system is shown in Figure 2.

FIGURE 1

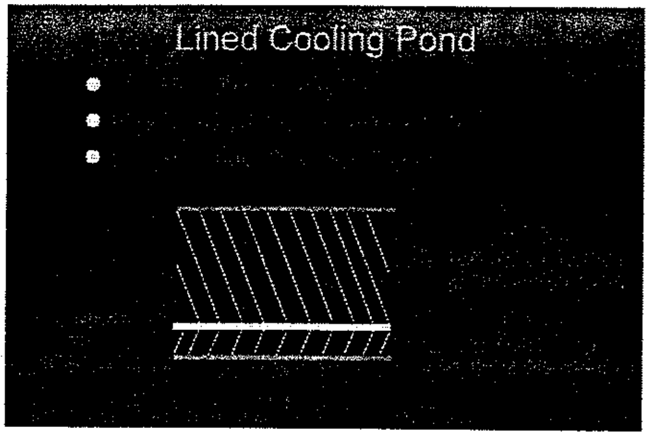
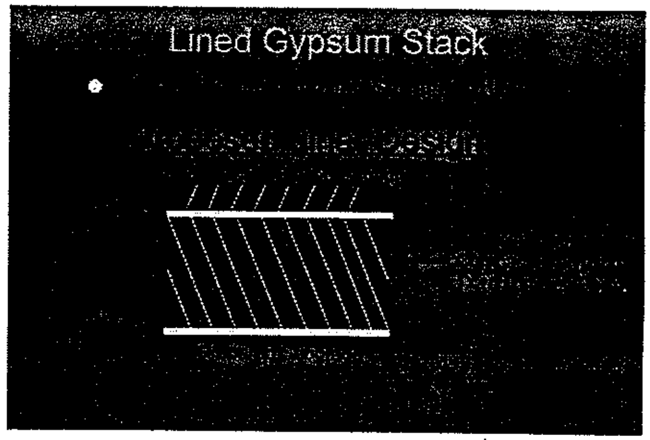


FIGURE 2



CFI plans to install this system in three construction sequences approximately eight years apart for the purpose of delaying both the installation costs and the ecological impacts. Following the initiation of gypsum storage in the first sequence, the capping of the existing unlined system will begin, initiating the elimination of the source of groundwater contaminants.

MINIMIZE PROCESS WATER CONTAMINATION

CFI believes any strategy in dealing with pond water inventories can be facilitated by reducing the contaminants in the process water long before final closure. The most obvious benefit would be reduced treatment cost for discharge, or more importantly, reduced pretreatment cost prior to the reuse or recycling of this water to displace well water at some future time. Several capital projects which follow this strategy have been implemented or are in the early planning stages. These projects include:

- **Process water separation & new lined cooling pond (Complete)**
- **RO system to reduce demineralizer waste (Partially Implemented)**
- **A sulfuric wash reuse project for the granulation plants (Complete)**
- **Double filtration (Planning)**

Process Water Separation

The process water separation project was completed in conjunction with the new lined cooling pond at a combined cost of $15 MM. The project converted a commingled gypsum stacking water and process water system into two separate recirculated water systems. All gypsum transport water is supplied by the gypsum stack water system. The water is supplied from a perimeter water ditch which collects seepage water and decanted water from the gypsum settling ponds. In addition to gypsum transport water, cooling tower blowdown and abatement water from the granulation facilities are returned with the gypsum to the top of the gypsum stack. Over time the addition of slightly contaminated fresh water with the gypsum slurry helps flush out the gypsum stack and lower the mean levels of contaminants.

The new lined cooling pond supplies all other process water needed throughout the Complex. The process water is used for barometric condensers, scrubbers, and miscellaneous cleaning. The process water is also the primary water being consumed into the process for wet rock grinding and filter cake wash water. All plant P_2O_5 losses and contaminants, except for filter losses, report to the new lined cooling pond. Fluoride from the barometric condensers and scrubbers, sulfates from sulfuric acid, and other chemical contaminants all enter the new lined cooling pond. Because of the large volumes of water lost from the cooling pond through process heat evaporation and process consumption, a continuous blowdown from the gypsum stack water system into the new cooling pond is required for make-up.

This project does not reduce the flow of contaminants into the process water, but the consumption of the contaminants recycled to the process is increased. This occurs by concentrating all sources of contaminants, except for the filter losses, into a single 310MM gallon lined cooling pond. Both water systems will develop new equilibrium concentrations of contaminants. Because all of the scrubbers and barometric condensers report to the new lined cooling pond, the concentration of fluorides is expected to increase and pH should fall. In the gypsum stack water system the pH is expected to rise and the fluoride concentration should drop because the only fluoride input is from the filters. Similar predictions can be made for all the process water contaminants, see Figures 3-6.

The separation of the two water systems, has resulted in an increase in suspended solids in the new cooling pond, see Figure 7. The new cooling pond became turbid while the visibility of the gypsum transport water improved slightly. The suspended solids are composed of >95% silica and are colloidal in nature. Pictures of the new cooling pond resemble the muddy Mississippi while the gypsum stack water retained its normal dark color, see Figure 8. This phenomenon is still being evaluated to determine if there are any adverse effects on filtration systems, attack systems, or process equipment scaling.

FIGURE 3

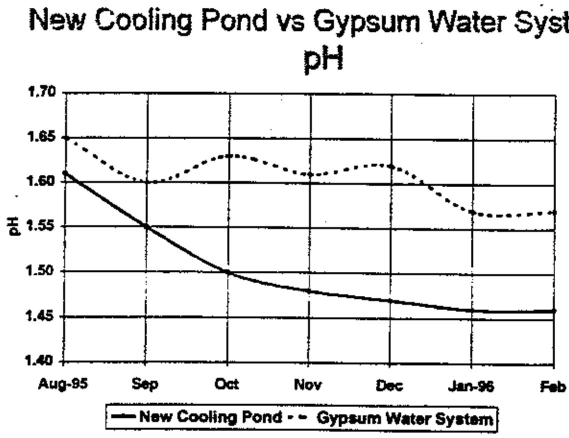


FIGURE 4

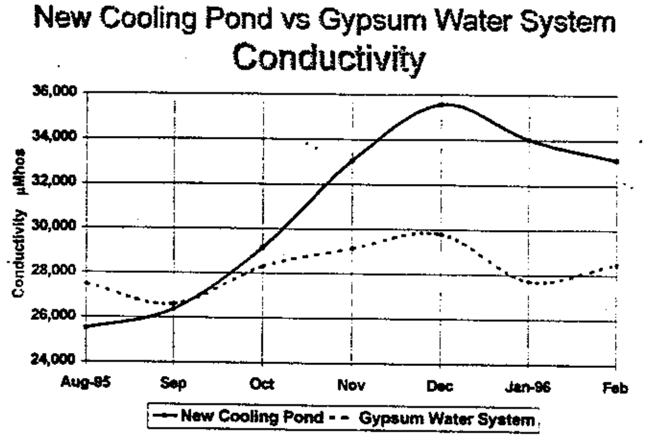


FIGURE 5

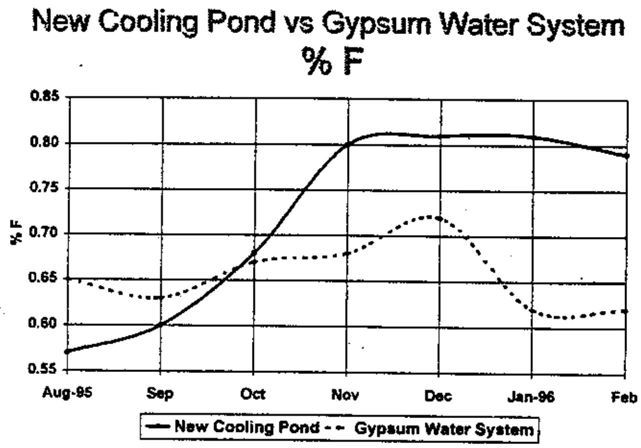


FIGURE 6

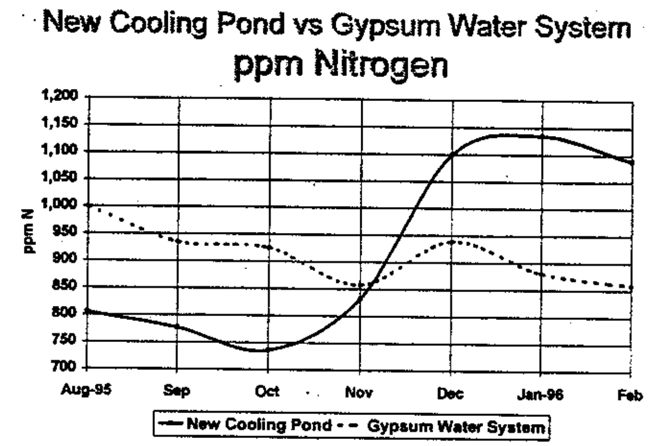


FIGURE 7

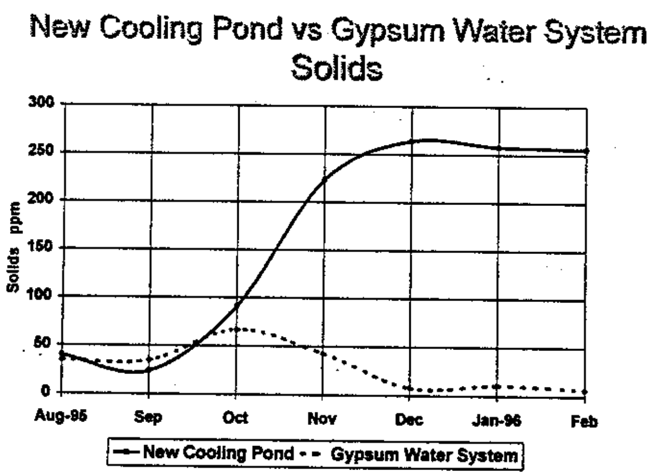
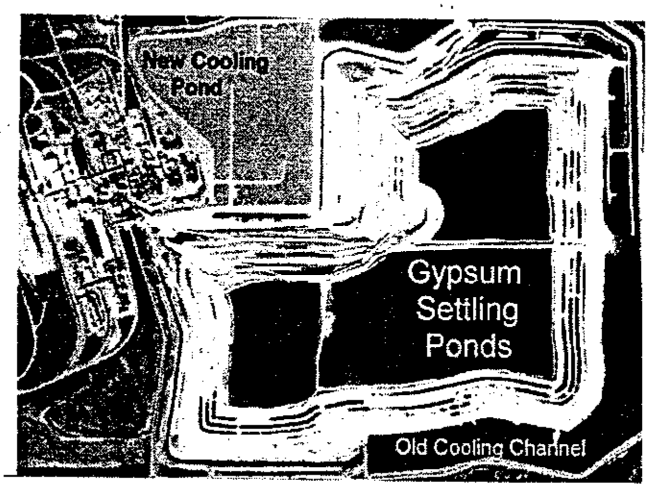


FIGURE 8



As a final note to this project, I would like to talk briefly about CF's decision to go with a new lined cooling pond instead of cooling tower. The new lined cooling pond clearly costs more to install and carries the liability associated with storing process water. However, the new cooling pond was selected because of its large water surge capacity, lower maintenance cost, and lower fluoride emissions. Because evaporation exceeds rainfall, the increased rainshed associated with the 80 acre cooling pond does not negatively impact the water balance and should not be a disadvantage as compared to pond water cooling towers.

Reverse Osmosis

For several years, sulfuric acid waste from sulfuric acid plants and granulation plants was exempt from EPA's classification of hazardous waste. But more recent interpretations of the Clean Water Act's Bevill Amendment no longer exclude the sulfuric acid wastes generated outside the phosphoric acid plant. In response to this, CF has implemented two capital projects to deal with these wastes.

In the sulfuric acid plants, sulfuric and caustic wastes are created during regeneration of demineralizer ion exchange resins. To significantly reduce these wastes, a 500GPM portable reverse osmosis (RO) unit was leased to pre-treat demineralizer feed water. The RO system was designed to remove 97% of the dissolved solids from the water before demineralization, thereby reducing the conductivity from over 1000μMHOS to less than 50μMHOS. The RO system reduced the regeneration cycles from 13.3 times per day to 2.5 times per day, and reduced the volume of sulfuric and caustic waste by 80%. Because the leased RO system only supplies about 90% of the current demand for demineralizer feed water, the low conductivity RO permeate must be supplemented with untreated higher conductivity deep well water. This results in regeneration wastes that could be avoided with more RO capacity. The remaining 20% of the sulfuric acid regeneration waste is recycled by transferring it to the phosphoric acid plants and using it for scrub solution in evaporator cleanings.

CFI is currently seeking approval for a 1,000GPM RO system to replace the currently leased unit. The increased capacity of the permanent RO system will be utilized to replace softened water currently being used for dilution and scrubber water in two single absorption sulfuric acid plants. The capacity of the new unit is designed to adequately supply total peak demand for demineralizer feed water, acid dilution water, and scrubber water. Because the new unit is sized to meet peak demand, the number of required demineralizer regenerations is expected to be less than 0.5 per day. Small volumes of waste created from demineralizer regenerations will then be mixed with RO permeate and used for sulfuric acid dilution water.

A second issue associated with RO use is its impact on complex process water balance. Typical RO units operate with a 70% to 80% recovery. This means that 70% to 80% of the RO feed is processed into low conductivity permeate and the remaining 20% to 30% ends up as high conductivity concentrate. The RO concentrate is discarded to the process water system and negatively impacts the water balance. The water balance impact is partially offset by a reduction in demineralizer regeneration wash water but could still result in 50-100 GPM of extra water entering the water balance.

To eliminate this problem CFI's RO systems are specifically designed for high recovery. The currently leased RO system and new permanent RO system are designed for an 88% recovery. With an 88% recovery the reduction in demineralizer regeneration wash water is greater than the volume of RO concentrate thereby producing a beneficial impact on the complex water balance. The reduction in deep well withdraw and impact on water balance are estimated to be 34 gpm for the new permanent RO system.

Over time, the RO project is expected to reduce the overall toxicity and volume of process water in the cooling ponds and in the gypsum stack system. The levels of acidity, sulfates, sodium, and chlorides in the process water are all expected to be reduced by this project. In addition to the reduction in contaminants, the reduction in caustic, sulfuric acid, salt, and resin expenses provide the economic justification for the RO project.

Sulfuric Acid Scrub Solution Reuse

Historically, the granulation plants have utilized a mixture of 5% sulfuric acid in process water as a scrub solution. As part of the review of waste discharges to the process water system, it was determined that approximately 3600 TPY of sulfuric acid was being consumed for this purpose. Clearly, the elimination of this sulfuric acid use had economic as well as environmental benefits.

The elimination of this sulfuric acid use was achieved by collecting evaporator scrub solution, which consisted of condensate and 5% sulfuric acid, and reusing it in the granulation plants. This project was successfully implemented in 1994 and the reused solution has proved to be superior to the old scrub solution. The elimination of the 3600 TPY sulfuric acid discharge to the process water system is a significant environmental benefit.

Second Stage Gypsum Filtration

The effect of separation of the cooling pond system from the gypsum stacking system was to isolate the source of contamination to the gypsum stack to only the cake discharge from the filters. With this accomplished, the major input of contaminants is represented by the liquid phase of the filter cake plus impurities which dissolve from the gypsum.

To further reduce the contaminant load to the gypsum stack filtration efficiencies must be improved. The most effective method of reaching this goal is believed to be the transporting and refiltration of the gypsum. This approach would reduce normal operating of water soluble P_2O_5 to the system and also mitigate the input from startups, shutdowns, and process upsets. Plant testing by Jacobs Engineering under a FIPR grant has been published and indicates the water soluble P_2O_5 input to the stack could be reduced by 80% - 90%.

CFI has completed bench scale testing which indicates that the combination of process water separation and second stage filtration could reduce gypsum stack water P_2O_5 content to approximately 0.2% or less. This benefits P_2O_5 recovery as well as further reducing any future process water treatment or pre-treatment costs. CFI hopes to implement this concept in the future.

CONTROL OF PROCESS WATER INVENTORY

The control of process water inventory within available storage is the primary goal of any process water management plan. The first requirement of inventory control is an understanding of the total complex water balance and water uses. A water balance and water use inventory serve two separate functions. The water balance deals with water inputs and outputs and allows the prediction of how the overall process water inventory will change given a particular set of operating assumptions. The water use inventory tells you how and where water is used in the complex and where management opportunities exist to reduce input to the process water system.

Water Balances and Inventory Measurements

A summary of typical water balance outputs and inputs for CF Industries' Plant City Complex is shown in Figure 9. These water balances have taken an overall view of the Complex which includes plant stacks, cooling towers, etc., rather than focusing only on the process water system. The method looks at water inputs and outputs which are directly measured or can be reliably calculated and assumes any difference is the effect on inventory. Typical rainfall accounts for 21% of total water input as compared to 68% for deep well pumping. Looking at the process water system by itself, rainfall represents 53% of the total while well water accounts for 47%. These numbers show the importance of managing input of well water to the process water system.

A recent example of the application of the water balance model was the new process water cooling pond construction time period. We were able to predict how inventories would change over time and show that construction site dewatering could be contained within the available storage capacity. Containment of rainfall in the process water system was required since the construction site had been used as a lime settlement area in past years and rainfall or seepage would be contaminated. Periodic physical inventories of process water are completed to assist in confirming water balance projections. The comparison of physical inventory to predicted inventory is shown in Figure 10.

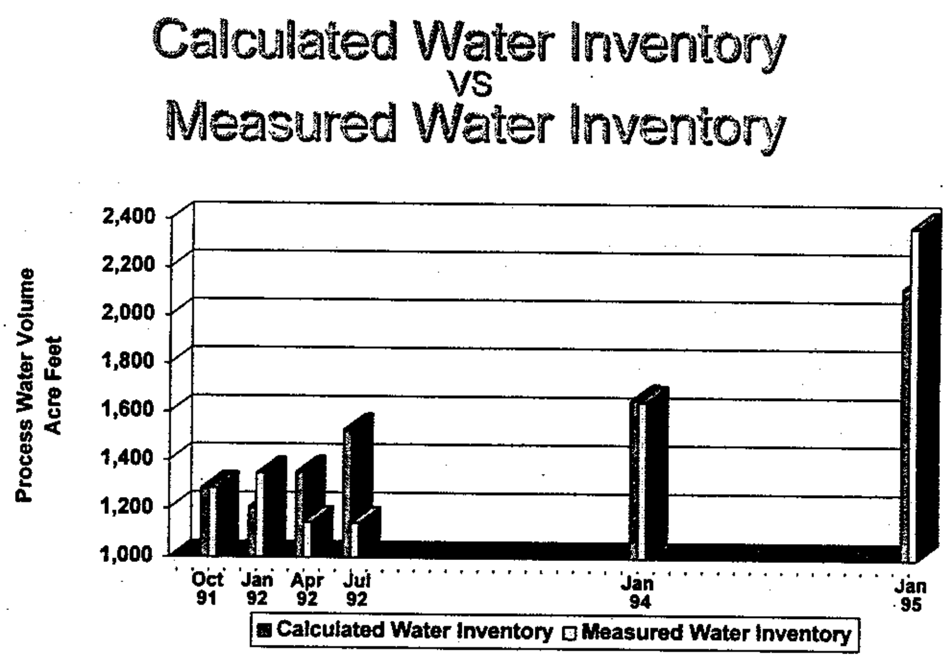
FIGURE 9

Water Balance Inputs & Outputs

INPUT DESCRIPTION	
Total Well Water Pumped	
Total Complex Rainfall	
Ground Water Remediation	
Water From Non Process Ponds	
Raw Material Water Input	Wet Rock
	Imported H2SO4
	Imported P2O5
	Ammonia
	Additives
	CH4 Combustion
Plant Stacks Inputs	A-SAP
	B-SAP
	C-SAP
	D-SAP
	A-PAP
	B-PAP
	A-DAP
	X-DAP
	Y-DAP
	Z-DAP
	Storage
Total Input	

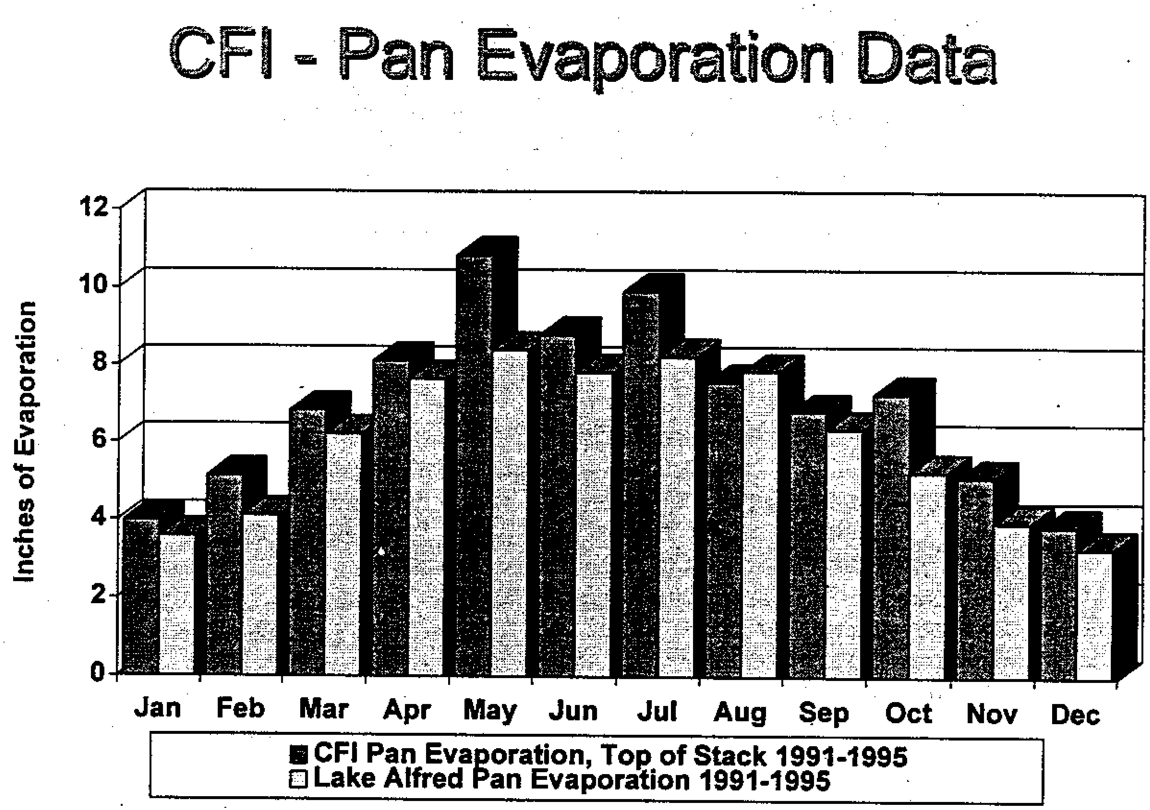
OUTPUT DESCRIPTION	
Process Heat Evaporation	
Gypsum Losses	Chemical
	Free Water
Gypsum Stack Evaporation	Upper Ponds
	Lower Ponds
	Evapotranspiration
Cooling Tower Evaporation & Drift Losses	A-SAP
	B-SAP
	C-SAP
	D-SAP
	TG
	Total Drift .02%
Plant Stack Outputs	A-SAP
	B-SAP
	C-SAP
	D-SAP
	A-PAP
	B-PAP
	A-DAP
	X-DAP
	Y-DAP
	Z-DAP
	Storage
Product Water	DAP
	MAP
	GTSP
Chemically Reacted Water (H2SO4)	
GTSP Chemically Bound Water	
Misc. Vented Steam	
Discharges To Effluent System	
Complex Water Seepage	
Total Output	
Calc. Water Inventory	
Actual Measured Inventory	

FIGURE 10



Water balances are an evolving art since many of the factors such as evaporation, evapotranspiration, seepage, gypsum stack pore water, are constantly being refined. Early water balance models suggested that process water evaporation rates might be higher than assumed. To confirm this, a four year pan evaporation measurement program was completed at the Plant City Complex. This testing involved test pans for both process water and fresh water located at grade and at the elevation of surge ponds on top of the stack. Process water evaporation rates have historically been measured at about 5% above published lake evaporation rates. The new data has found that evaporation rates on the elevated ponds are significantly higher than those used in previous balances. With the elevation of the Plant City ponds at approximately 175 feet above grade, surge pond evaporation rates of 15% were typical. The results of this study are summarized in Figure 11.

FIGURE 11

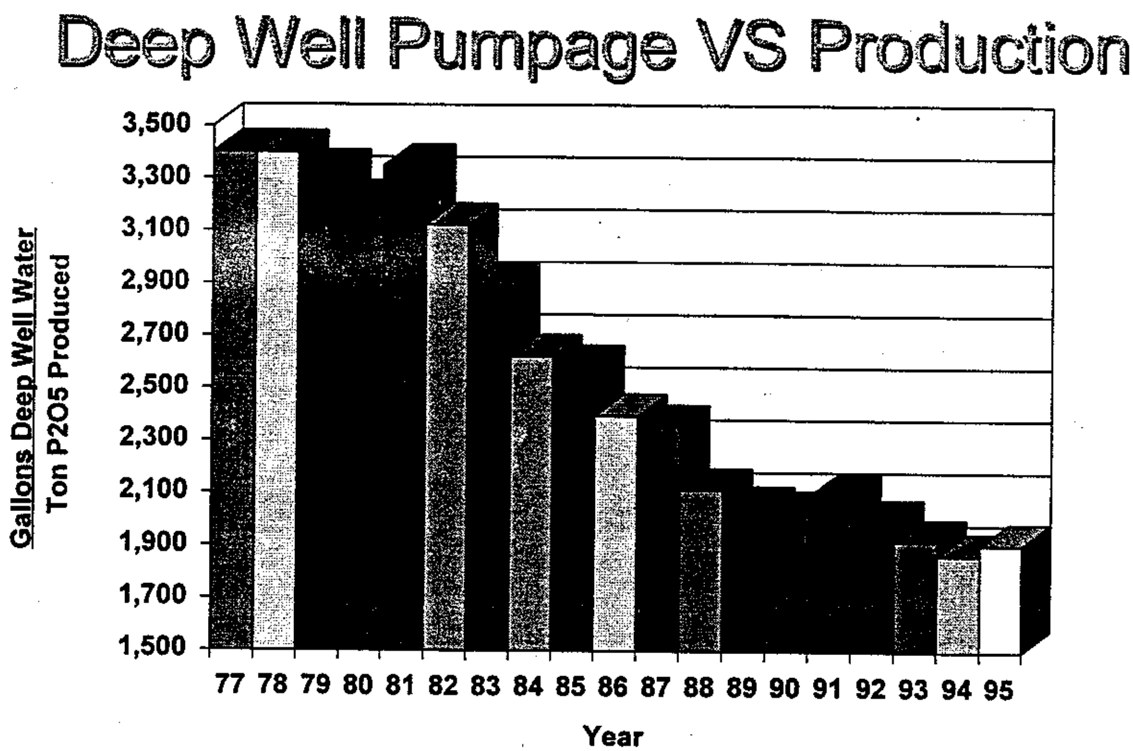


Existing Water Reuse Practices

The Plant City Complex consumes approximately 5 MGD of well water each day. Much of this water is reused several times before it finds its way to the process water system. An overall water supply demand of 6.5 MGD has been estimated from a survey of water consumers. The affect of this water reuse has been to reduce the rate of deepwell water consumption at the Plant City Complex from approximately 3400 to 1900 gallons per ton P_2O_5

produced. Historical water consumption rates are illustrated in Figure 12.

FIGURE 12



As new capital projects are added at the Complex, water use and reuse is a key issue. Recently, additional scrubbers were added to the existing granulation plants to improve fume and dust collection. To prevent the need to add to the total stack gas flow the dryer quench air stream was used as the available air collection volume. Additional fume and dust collection points were added using this volume and the gas fed to a new scrubber which cleaned the gas before it was fed to the dryer as quench air. Since existing dryer fans and dryer air preheater equipment were carbon steel, some form of fresh water scrubbing would be required to clean the gases before being used as quench air. This was achieved by a combination of once through pond water scrubbing followed by a recirculated fresh water system to remove any acid or scale forming tendencies of the gas stream.

Future Water Reuse Practices

Several factors are currently moving the Plant City Complex to make major changes in its water supply and distribution systems.

First, the Plant City Complex entered into a Consent Order with DEP in 1987. The results of this Consent Order will be the installation of six remediation wells which will recover contaminated groundwater. This water must be incorporated into the site water balance to displace an equivalent volume of well water to avoid an adverse impact on the plant water balance.

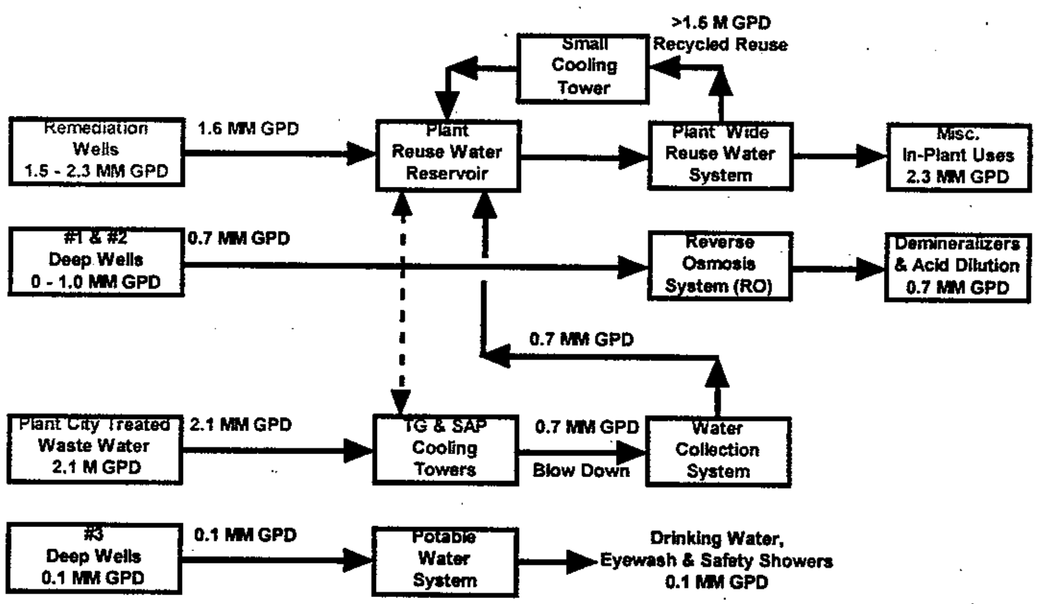
Second, CFI entered into an agreement with the City of Plant City to take approximately 2 MGPD of treated wastewater for use in cooling towers. This water will be treated to the level to make it "Public Access Reuse Water" which should work well in the three cooling towers.

Third, the Plant City Complex is in the process of expanding its gypsum stacking capacity and preparing to close the existing stack. The construction of the stack expansion will require significant management of current water inventory which has increased due to the recent cooling pond construction project. In addition, the Complex is committed to the early closure of the existing stack which will require the incorporation of stack seepage into the plant water balance.

To accomplish these goals several capital projects are being implemented. First, a new potable water system will be installed to separate the potable water system from the existing plantwide water distribution system. Second, a new water supply system to connect the City of Plant City wastewater supply pipeline to the three cooling towers will be installed. Third, the existing plantwide water distribution system will be converted to a centralized water reuse system with makeup from the remediation wells. The future configuration of the Complex's water supply system is illustrated in Figure 13.

FIGURE 13

CF Industries - Plant City Phosphate Complex
Future Water Systems



The major feature of the new centralized water reuse supply system will be the increased ability to reuse water over and above current water reuse levels. The effect will be to reduce groundwater pumping from the current average 5.2 MGPD to 4.5 MGPD or less. This reduction in water use will result in a direct reduction of water input to the process water system of 700 gpm or approximately 1000 ac-ft per year. To put this reduction in perspective it represents an effective decrease of 19 inches per year of rainfall to the process water rainshed. This central system will provide the management tool needed to facilitate closure of the existing stack and any future stack.

SUMMARY

The concept of process water management is key for all phosphate chemical plants. The concepts presented in this paper provide an example of one set of solutions to improved process water management. This is a long term commitment which will enable CFI to ensure no discharges of process water occur and closure of existing and future gypsum stacks can be accomplished in a practical, low cost fashion. It is CFI's intent to develop a strategy which will allow a step wise, or "close as you go" approach to gypsum stacks and their associated process water.