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REVERSE OSMOSIS OF PHOSPHATE PLANT POND WATER BY USE OF NOVEL PRE-TREATMENT TECHNOLOGY

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Phosphate plant pond water or process water is an acidic mixture of many ions and saturated with many compounds. In a wet process phosphoric acid plant the pond water is used for washing the calcium sulfate (gypsum) filter cake, for cooling and scrubbing process vapors, conveying the gypsum to the stacking area and other purposes that do not require fresh water. In an operating plant this water is normally recycled and the discharge of water is not necessary. However, during extended periods of heavy rain or when a plant is shut down, as in the case of Piney Point, this acidic water must be treated and discharged. The traditional method of treating pond water has been lime treatment in two stages (double liming). However, double liming suffers from several disadvantages. Large settling ponds are required for the second stage solids separation, and only about 50-60% of the water ends up being discharged, but even after lime treatment, air stripping is often required to reduce the ammonia concentration to acceptable levels.

Normally the major acidic components of pond water are phosphoric acid and sulfuric acid, with lesser amounts of hydrofluosilicic acid (H_2SiF_6), and hydrofluoric acid (HF). In an operating phosphoric acid complex, the pond water is normally saturated or supersaturated with respect to many of the ions contained within it. The only exception to this statement would be immediately after a period of extremely heavy rainfall. Also, since the pond water is used for cooling it is continuously thermally cyced. This thermal cycling, along with the addition of some waste fresh water to the pond water is why the pond water can function as an effective scrubbing fluid for some process gasses.

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While it cannot be said that there is any typical composition for pond water some of the major chemical components that could be found in pond water, and an example of their range of concentrations, are as follows:

CHEMICAL COMPONENT	RANGE OF CONCENTRATION
P	1700-12,000 ppm
SO_4	4300-9600 ppm
F	50-15,000 ppm
Si	10-4100 ppm
(ammoniacal) N	40-1500 ppm
Na	1200-2500 ppm
Mg	160-510 ppm
Ca	450-3500 ppm
K	80-370 ppm
Fe	5-350 ppm
Al	10-430 ppm
Cl	10-300 ppm

In many cases, in an efficiently operated phosphoric acid plant, in the absence of severe weather conditions, a balance will exist between water input to the pond system and water evaporation such that virtually all of the pond water can be recycled and used within the plant. In this case, treatment and discharge of the contaminated pond water is not necessary.

One method of treating pond water that has, until now, been the industry standard is double liming. This method consists of adding a calcium compound (such as $CaCO_3$, $Ca(OH)_2$ or CaO) to the pond water, in two stages, such that the phosphate and other impurities form precipitates that settle and are separated from the liquid phase. During the first stage lime treatment, to a pH of about 5.5, fluorine is precipitated as CaF_2 and/or $CaSiF_6$. As the pH rises to about five much of the hydrofluosilicic acid present dissociates to HF and SiF_4, with the SiF_4 hydrolyzing to HF and SiO_2. Some phosphate is also precipitated at this stage as $Ca_3(PO_4)_2$, hydroxyapatite. The sludge (CaF_2, $CaSiF_6$, $Ca3(PO_4)_2$ and other compounds) produced at this stage is a granular, crystalline material that settles fairly rapidly and can be de-watered to about 30% solids in a gravity thickener. The sludge can be sent to the plant gypsum stack or recycled to the phosphoric acid plant for recovery of the phosphorus. In the second stage, additional lime is added to the clear liquid from the first stage to a pH of about 11 – 12. In this stage the remaining phosphates and fluorides are precipitated along with sulfate and many of the metals. The sludge in this stage has poor settling and thickening properties, due to the hydroxide nature of many of the compounds, and rarely achieves more than 5% - 7% solids by weight. The sludge from this stage is normally deposited in large lagoons to allow for additional de-watering. Typically, however, this clarified water from the second stage is still not capable of being released to the environment. This is because the water usually still contains ammonia in excess of the allowable concentration for discharge. Thus, common practice is to airstrip the ammonia by spraying the water into the air and allowing it to fall back into the ponds. Overall, the quantity of clear water that can be obtained from a double liming process is only about 50% of the feed volume.

THE PRE-TREATMENT TECHNOLOGY

Reverse osmosis has long been viewed as an attractive alternative for pond water remediation, and over the last decade or so, many attempts have been made to use this technology. However, because pond water is already a saturated solution, the early attempts always resulted in rapid and irreversible fouling of the R.O. membranes. Also, even when the pond water was from a closed plant where rainwater had diluted it below saturation levels, an R.O. system can only remove a relatively small amount of purified water from the pond water before it again becomes a saturated solution. Thus, it was recognized that successful R.O. treatment of pond water requires some form of pretreatment.

In our reverse osmosis pretreatment process, the objectives are to remove only those ions that will cause solids precipitation from the pond water when it is concentrated and to keep as much of the phosphate as possible in solution. Thus, while some lime is added to the pond water as part of the pretreatment, the quantity is much less than would otherwise be used even in the first stage of the double liming process. This results in a much smaller volume of sludge being generated when compared with double liming, and a significantly higher solids concentration (>40%) in the resultant sludge. Also, since the majority of the phosphate is retained in solution during the pretreatment process, the reject or concentrate from the R.O. system can have significant economic value, either as a liquid fertilizer or as an additional feed stream to an operating phosphate fertilizer plant. Another advantage of our pretreatment process is that, with some pond water feeds, a second by-product can be produced that can have economic value. Overall, the final permeate yield that can be obtained using our pretreatment process followed by a two pass R.O. has been demonstrated as high as 75% of the initial pond water volume. Furthermore, the R.O. permeate can easily meet Florida Class III Fresh Water Standards and Drinking Standards in terms of purity. The following table shows the results obtained with pond water from the Uncle Sam, Louisiana phosphoric acid plant.

	Raw Pond Water	R.O. Reject	R.O. Final Permeate
P_2O_5	1.61%	5.65%	0.23 ppm
CaO	0.167%	0.060%	0.1 ppm
F	0.470%	0.038%	0.83 ppm
SiO_2	0.440%	0.079%	1.0 ppm
Na_2O	0.310%	2.85%	8.1 ppm
SO_4	0.440%	2.83%	12 ppm
NH_3 - N	0.200%	--	0.80 ppm
Conductivity (umho/cm)	19,800	--	59

Another objective during the development of our pretreatment process was low cost. This objective has also been achieved with the operating cost of our process (pretreatment plus R.O.) being 25% to 30% lower than a comparably sized double liming plant and the capital cost for a new "green field" plant estimated to be about 15% lower than a comparably sized double liming plant. Furthermore additional cost savings can be achieved if the proposed site already has a double liming plant, since some of the equipment from the double liming plant can be modified and used in our pretreatment process.

THE PROOF OF THE PUDDING

As stated we have developed a pre-treatment method that allows phosphate plant pond water to be treated using reverse osmosis without the usual scaling problems, upwards of 75% of the water can be discharged; the discharge water is of exceptionally high quality; up to 75% of the P_2O_5 in the water can be recovered as a non-scaling liquid and operating costs are lower than double liming. Our process is flexible and can be adapted to dilute pond water, such as at Piney Point, or more concentrated pond water, typically found at an operating phosphoric acid plant.

In order to commercially demonstrate the economic and technical viability of this pre-treatment technology, we approached the Department of Environmental Protection in Florida and the Court appointed Receiver for the bankrupt and idled Mulberry Phosphate Piney Point phosphate facility for an opportunity to help remediate their large store of pond water. Presentations to the Florida Institute of Phosphate Research resulted in an award of $900,000 to facilitate the construction of a plant to demonstrate the production of water suitable for discharge from the Piney Point facility in Manatee county Florida.

The formation of an IMC global subsidiary, "Pure Water Technologies Holding Company LLC", allowed us to form a joint venture, "Florida Pines Water Venture LLC", with "Mobile Process Technology" who was skilled in the art of wastewater remediation and in Reverse osmosis. Florida Pines JV entered into a contract at Piney Point on October 6th, 2003 to produce 800,000 gallon per day of dischargeable water over a 105 day period following a 12 week construction period. Suffice it to say, it took 17 legal agreements to be able to move forward at this abandoned facility, (Thanks Marian and Jim). At this time, mid January 2004, the plant is almost ready to be commissioned, and the presentation in Beijing will additionally describe the results of our efforts.

The efforts and support of the personnel in IMC Phosphates Technology Development Group, Mobile Process Technology, DEP, FIPR and our Corporate E, H&S were invaluable.