Case Study - Gypsum Stack or Gyp Stack Treatment Solution

What is this Impossible Wastewater and Where does it Come From ?

70% of the U.S. Phosphate ore is mined in central Florida. This material is processed to make phosphoric acid fertilizer which is the building block for phosphate fertilizers. During the chemical conversion, huge amounts of acidic wastewater is generated and is stored permanently in storage ponds called phosphogypsum stacks or gypsum stacks.

There are three steps in the process:

- Mining where sand, clay, and phosphate pebbles are slurried for transport
- Beneficiation - floatation & screening remove unwanted materials and concentrate ore
- Processing – Sulfuric Acid is added to convert calcium phosphate to phosphoric acid

Calcium phosphate+Sulfuric acid→Phosphoric acid+Calcium sulfate (gypsum)

Calcium Sulfate (gypsum) is clarified and removed as a slurry and transported to the gypsum stacks. Large volumes of water are added to keep the gypsum solids moving. Gypsum solids are also washed to recover more phosphoric acid generating more wastewater. For every ton of phosphoric acid that is produced, 5 tons of gypsum effluent is generated. This acidic (pH 2-4) wastewater is enriched in phosphate, fluoride, sulfate, ammonium, trace metals, and naturally occurring radioactive materials such as uranium.

A gypsum stack is a hydraulic storage system to hold this acidic wastewater. It is often recycled to the plant to be used as cooling water, but it is basically stored indefinitely and volumes increase with time. Earthen berms are used for above ground storage ponds and the dikes are raised progressively as more waste arrives.

High levels of phosphorous and the low pH make this problematic for discharge. Emergency releases have been done during a Piney Point episode and this caused extreme algae blooms near Tampa. This gypsum stack water is also classified as “technology enhanced naturally occurring radioactive material” (TENORM). It contains 5-50 pCi/L of Radium 226 and Radium 228 as well as 5-10 mg/L of uranium. It also contains daughter nuclides radon and polonium.

Why this Water is Difficult to Treat.

Gypsum stack water is low pH, prone to fluoride scaling and calcium scaling, high in gypsum and suspended solids, and has low level radioactivity. If this water was easy to treat, it would have been treated by now. As this wastewater accumulates, there are now massive amounts of permanently stored acidic wastewater. There is about 265 billion gallons of gypsum stack wastewater stored in 25 ponds in Florida. 7 billion gallons of new wastewater are generated every year.

Conventional spiral RO membrane, that were tried, failed rapidly due to scaling and plugging issues. Lime treatment has been done, but this generates massive amounts of sludge. Evaporation can work but is energy intensive and given the volumes involved, this would not be practical. Assuming 100% heat transfer, it would take a minimum of 647 TWh of energy which is three timed to total energy consumption of the State of Florida. A 1 GW nuclear power plant can generate 8 TWh per year.

Risks to the Environment

Piney Point was a former processing plant that ran for 33 years and closed in 1999 leaving hundreds of millions of gallons of gypsum stack water in aging ponds. It is now being managed by the State. In 2021, a tear in the liner at the base of one of the gypsum stacks caused a leak. This leaking gypsum stack nearly collapsed before an emergency release of wastewater was sent to tidal waters of Tampa Bay. The choices were not good. If allowed to fail, the gypsum stack would have released hundreds of millions of gallons at once, would have flooded local residential neighborhoods, and could have destabilized adjacent gypsum stacks. In April, the Florida Department of Environmental Protection approved an emergency release. This resulted in 22,000 gpm of this wastewater being pumped into tidal waters of Tampa Bay resulting in total release of 215 million gallons. This resulted in a severe red tide algae bloom and massive fish kills. This episode demonstrates that gypsum stacks cannot be left indefinitely without remediation.

A Solution has been Proven but not Adopted.

The Florida Institute of Phosphate Research (FIPR), a state funded agency provided a grant to New Logic Research to demonstrate the use of its VSEP® RO technology to filter and treat this Phosphogypsum wastewater. The research focused on scaling resistance and shear enhanced filtration of acidic wastewater at a gypsum stack in Florida.

The VSEP® system was tested using Piney Point gypsum stack acidic wastewater in 2005, long before the emergency breach and subsequent discharge of millions of gallons. During the FIPR funded testing, the VSEP® used a RO membrane and recovered 65% of the volume a filtrate in a stage one process and then another 75% a filtrate in stage two. This resulted in a 92% overall recovery or volume reduction. Because the starting levels of dissolved solids were high, two stages of conventional spiral RO polishing were used to make ultraclean water suitable for discharge.

Parameter	Limits	Feed	VSEP® Permeate	Spiral RO Perm	Spiral RO 2 Perm
Fluoride	5.0	66	37	23	4.6
Ammonia	1.0	370	30	1.4	0.1
Nitrogen	2.0	450	16	2.0	0.3
Phosphorous	0.5	1,030	13	0.4	0.0
Dissolved Solid	50.0	8,260	120	40	13

Units are mg/L

Uranium was not tested, however, aluminum and magnesium were tested and were reduced by 99.99%. It can be assumed that Uranium and daughter nuclides would be similarly reduced. The VSEP® ® RO System performed with no scaling or fouling and achieved a flux rate of 30 GFD (50 LMH)in stage one and 12 GFD (20 LMH) in stage two.

VSEP® is a Membrane that can work for Phosphogypsum Wastewater

Spiral RO membranes rely on laminar crossflow to create shear and turbulence to limit fouling. But the shear from simple laminar flow is not enough to prevent crystallization from causing scaling of the membrane. In spiral RO systems the solids become concentrated at the membrane surface and this is known as concentration polarization. In a spiral system, the solids can be 10-20 times more concentrated at the membrane surface than in the bulk flow. For this reason they are limited to waters that are below their solubility limit and cannot crystalize. Gypsum stack water is super saturated and is not suitable to feed to a spiral system, even with pretreatment.

The VSEP® (vibratory shear enhanced processing) RO membrane employs torsional oscillation of the membrane with a cycle frequency of 50 times per second. This generates enough shear at the membrane surface to disrupt concentration polarization. The shear and agitation also disrupts crystallization where the shear is highest. There I a shear decay length as you depart from the membrane and as the shear dissipates as you get out into the bulk flow, then crystallization can occur and does occur in the VSEP® system. This happens without scaling on the membrane, but with precipitation of solids in the bulk flow. In this way, the VSEP® works like a membrane crystallizer.

This can be seen in the image above. There is only slight turbidity in the initial wastewater shown in the middle. The final VSEP® concentrate measuring about 10% total solids has large amounts of precipitated solids settled on the bottom of the jar on the right. Additionally there are lots of precipitated small colloids that do not settle causing turbidity in the final concentrate.

A VSEP® system has been used at a phosphate fertilizer plant since 2000 for a different application. So VSEP® is known to the industry. For now, Phosphogypsum wastewater is just being stored, but when final remediation is needed, VSEP® RO can provide a viable solution for discharge.