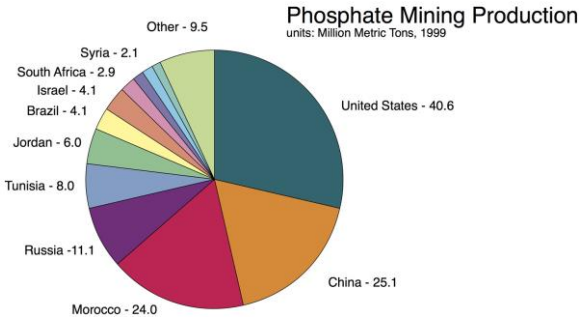
NEW LOGIC

Case Study

Case Study: Nanofiltration of Phosphoric Acid

Certain elements essential for plant growth and Phosphorous is one of them. Phosphate compounds provide energy for most of the chemical reactions that occur in living plant cells. Therefore, enriching soils with Phosphate Fertilizers enhances plant growth.

Phosphate mining is concentrated in areas where deposits of phosphorous exist and there are not that many places on the planet with good deposits. These places include Florida, North Carolina, Wyoming, Idaho, Ontario, Saskatchewan, Queensland Australia, Morocco, Senegal, and Jordan. These deposits vary a great deal in their composition. For example, deposits in North Carolina can have high levels of Organics (TOC). Deposits in Senegal can have high levels of Uranium.



Most of the Phosphate mined is used to make fertilizer for planting. This is known as Merchant Grade. Higher quality levels such as Technical Grade and Food Grade are used for more specific applications that require higher purity. No matter what the grade, the contaminant level of the Phosphoric product determines the value on the market. Because the Phosphorous is dissolved from the ore using Sulfuric Acid, many metals are extracted as well. Some of these such as Iron are also beneficial plant nutrients. However, some such as Arsenic, Cadmium, Lead, Molybdenum, Vanadium, and Uranium are not.

The process of mining Phosphorous ore involves first removing about 25' of overburden. The phosphate rock is removed using a dragline and is sent to a washer where large clay balls are pulverized and removed. The remainder passes through a shaker screen where sand and phosphate pebbles are recovered. This slurry is sent to a floatation basin where the sand and phosphate are separated. The sand is saved for reclamation and the phosphate is dewatered and stored in stockpiles. The stored phosphate rock is shipped by rail to the processing plant where it is finely ground to a uniform size and mixed with Sulfuric Acid. The result is Calcium Sulfate and Phosphoric Acid. The Calcium Sulfate (gypsum) is removed by clarification.

$$3\ H2SO4 + Ca3(PO4)2 + 6\ H2O = 2\ H3PO4 + 3\ CaSO4\text{-}2H2O$$

From here, the Phosphoric Acid can be processed into many things including animal feed enhancers and various grades of commercial Phosphoric Acid. The largest use is for fertilizer. In this case the Phosphoric Acid is reacted with Ammonia (a nitrogen source) to for Monoammonium Phosphate (MAP), Diammonium Phosphate (DAP), or Triammonium Phosphate (Liquid Poly-Ammonium Phosphate 10-34-0)

High purity Phosphoric Acid is produced by reduction with Coke in a high temperature furnace to produce elemental Phosphorous. It is then oxidized to make P2O5 and then dissolved in water to make Phosphoric Acid. This process is energy intensive and the operating costs are significant.

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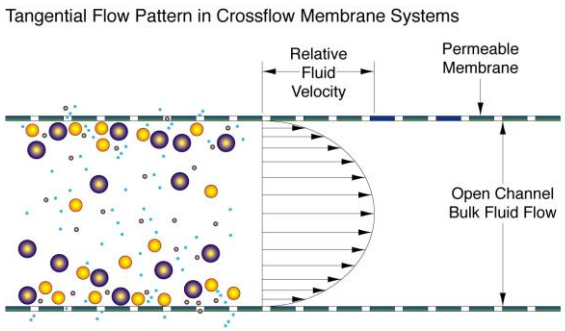
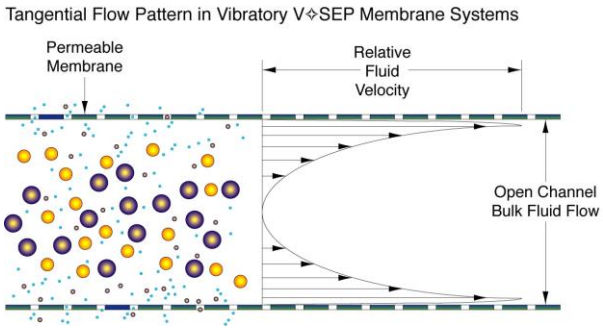
Methods of Phosphoric Acid purification are continually being studied as a way of getting better quality with reduced cost. When TOC is present, calcining can be used to destroy the carbon bearing organic molecules. Calcining involves baking the ore at extremely high temperature, so this process is also energy intensive. Another issue with this method is that the exhaust during this process can release Mercury into the atmosphere. Calcining does not remove most of the toxic heavy metals and is selective for TOC

The use of Polymeric membranes has been studied for many years. Membranes are desirable because they can remove all types of contaminants while allowing the Phosphoric Acid to pass through the membrane. The preferred category of membrane for this application is Nanofiltration, because the passage of Phosphoric Acid is nearly 100%, while the rejection of contaminant metals and organics is high.

Nanofiltration (NF) membranes are made in the same way as Reverse Osmosis (RO) membranes where a thin layer of Polyamide material is used as a top layer. NF membranes are often referred to as loose RO membranes and will allow more salt passage. However, the increased salt passage mostly applies to monovalent salts or very low molecular weight dissolved solids. Phosphoric Acid has a molecular weight of about 94 Daltons. NF membranes typical are sized to have rejection capabilities of between 150 and 800 Daltons. Ionic charge is also a factor in the rejection. So NF membranes will have good rejection for Divalent and Trivalent ions, especially metals and hardness.

While NF membranes can very effectively purify Phosphoric Acid, the main problem has been the fouling tendency and the high osmotic pressure due to concentration polarization of the membrane.





During membrane filtration, materials dissolved in the feed water are convectively driven to the membrane surface where the concentration of these materials increases to very high levels compared to the level in the liquid away from the membrane. This is known as concentration polarization and a boundary layer of highly concentrated dissolved solids forms near the membrane surface. Because the formation of the concentration polarization boundary layer results in increasing concentration of dissolved solids near the membrane surface, the osmotic pressure or pressure needed to be applied to for liquid passage increases. In addition, this region that has higher than normal levels of sparingly soluble salts may be subject to crystallization and scaling in very close proximity to the membrane surface. Therefore, the use of static or crossflow style spiral membranes will suffer from reduce flux rates and increased fouling with time.

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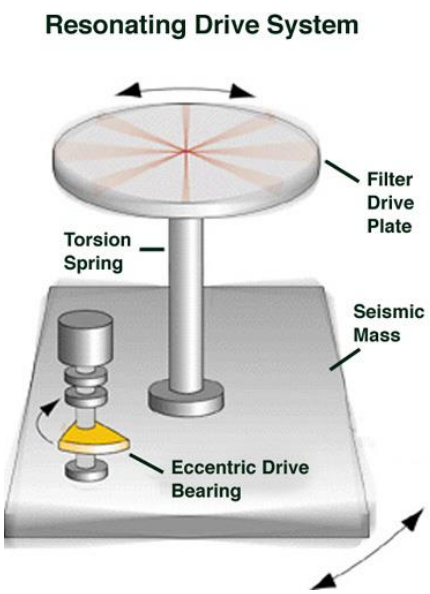

The formation of a cake layer on the membrane surface or a concentration polarization boundary layer near the membrane surface depends on the "back diffusion" rate during the filtration process. By vibrating the membrane surface to create higher shear rates than crossflow spiral membranes, the backwards diffusion can be enhanced. The back transport mechanisms of small molecular substances, macromolecules and colloids are all different. Large particles are preferentially back-transported by shear-induced waves of turbulence, whereas small materials are transported from the membrane by Brownian Motion diffusion. The back transport mechanisms also depend on the shear rate at the membrane surface. Using crossflow, or high laminar flow will have limited effect because of the drag at the membrane surface. The relative laminar flow is quicker away from the membrane and not as fast at the membrane surface. However, when the membrane is moved side to side and the liquid is relatively motionless, the shear at the membrane surface is much greater.

New Logic Research has developed a vibratory membrane technology for effective filtration of high TDS applications known as VSEP®. Dr. Brad Culkin invented the Vibratory Shear Enhanced Process (VSEP) technology in 1985. Dr. Culkin holds a Ph. D. in Chemical Engineering and was formerly a senior scientist with Dorr-Oliver Corporation. VSEP was originally developed as an economic system that would efficiently separate plasma from whole blood.

VSEP's unique separation technology is based upon an oscillating movement of the membrane surface with respect to the liquid to be filtered. The result is that blinding of the membrane surface due to the buildup of solids is eliminated and free access to the membrane pores is provided to the liquid fraction to be filtered. The shear created from the lateral displacement causes suspended solids and colloidal materials to be repelled and held in suspension above the membrane surface. This combined with laminar flow of the fluid across the membrane surface keeps the filtered liquid homogeneous and allows very high levels of recovery of filtrate from the feed material. The high rates of shear also enhance the effect of Brownian Motion whereby small dissolved solids are able to evenly migrate away from the membrane.

New Logic has deployed its VSEP technology many times to study the performance during filtration of Phosphoric Acid. Each case has had different objectives. In one case, the desire was to remove organics (TOC) as an alternative to calcination. In other cases, the desire was to remove heavy metals and toxins to improve the quality of fertilizer products. Another possible use is to remove Uranium and concentrate it to the point where recovery using selective ion exchange can be a method of Uranium recovery and production.

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New Logic has access to about 200 different membrane types. Of these some special NF membranes can be used that can tolerate the low pH and corrosive nature of the application. Phosphoric Acid is conserved a weak acid and so 316 stainless steel can be used for construction of the filtration system. Two primary NF membranes have been tested including one with a nominal molecular weight cut-off size of 500 Daltons and one with a cut-off of about 250 Daltons. The following table shows the relative rejection rates for each.

	500 da NF Rejection	250 da NF Rejection
Aluminum	77%	93%
Calcium	33%	60%
Cadmium	42%	82%
Chromium	70%	87%
Magnesium	74%	93%
Manganese	68%	91%
Nickel	58%	78%
Phosphoric Acid	0%	2%
Vanadium	63%	80%
Uranium	45%	65%
Zinc	47%	83%

Multiple passes through the same NF membrane may results in additional reductions. However, the use of membranes cannot reach the purity level required for food grade. NF membranes can be used though to increase the purity of lower grade acids and can make the mining of poor phosphate deposits more economical. Some ore deposits may not even be suitable for processing as the lowest grade Phosphoric Acid due to impurities. However, with NF filtration, these deposits can be processed.

Phosphoric Acid is typically produced at a concentration of 54%. Very high pressure is needed to get filtration to occur at that concentration. This acid can be diluted to between 18% and 30% where a more reasonable feed pressure of 500 psi (34 Bar) can be used. The lower the Phosphoric Acid concentration, the lower the osmotic pressure and the higher the flux rate will be. The dilute acid can then be sent to an evaporator to increase the concentration as desired.

Typically, a VSEP NF membrane module can provide about an average 20 GFD flux rate when the acid concentration is 18% The flux rate at an acid concentration of 30% is about 15 GFD. There are several applications in the Phosphate mining industry for VSEP. New Logic installed its first VSEP system for one application almost 20 years ago. The new applications that New Logic is exploring is the purification of Phosphoric Acid as described in this case study as well as the treatment of the Gypsum Pond water which is the effluent generated from the production of Phosphoric Acid.

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