Reclamation of Water and Sulfuric Acid from Spent Piranha Solutions and Piranha Generated Wastewater

(Task Number: 425.036)

Customized Project

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Cost Share (other than core funding):

- National Science Foundation, CBET Award

Objectives

Develop a commercially viable process for recovering water and concentrated sulfuric acid from piranha wastewaters

Context:

- Piranha wastewater flow rates are large ($Q \sim 100\ gpm$), and contain:

Sulfuric Acid, $[H_2SO_4] \sim 10 \frac{g}{l}$

Hydrogen Peroxide, $[H_2O_2] \sim 1 \frac{g}{l}$

Caro's Acid, $[H_2SO_5] \sim ?$

Peroxodisulfuric Acid, $[H_2S_2O_8] \sim ?$

Challenges:

- Sulfuric acid must be neutralized before RO can be used to recover water
- Acid and water recovery processes, like vacuum distillation, have an unattractive TCO

ESH Metrics and Impact

Accomplishing the research objective will reduced HVSM chemical demand, spare natural resources, make HVSM safer, and eliminate costs

- Reusing water reduces consumption of natural resources
    - Piranha wastes contain 50 – 95% water, depending on technology node and tool design
    - Each gallon of water reused eliminates a gallon of water demand
- Reusing sulfuric acid will:
  - Eliminate ESH-problematic materials
    - Purchased acids are highly concentrated, optimized for transport ⇒ minimum transportation cost
    - Recovered acid concentration will be optimized for reuse ⇒ minimum ESH risk
  - Reduce net chemical consumption
    - 1 kg of acid reused eliminates 1 kg of acid demand
    - 1 kg of acid reused eliminates 0.815 kg of sodium hydroxide demand
      - Sodium hydroxide is a chemical used in piranha wastewater treatment
  - Reduce discharge of ESH-problematic materials to the environment
    - 1 kg of acid reused eliminates the discharge of 1.45 kg of dissolved solids to the environment
      - Dissolved solids are an ESH-problematic material; they contribute to TDS
- Reduced chemical consumption, natural resource demand, and ESH risk translates to money saved

Research Differentiators

The proposed process employs a modified form of electrodialysis (ED) to recover water and concentrated sulfuric acid, offering distinct advantages over processes predicated over distillation

Pros:

- ED is a cost effective option for high volume brackish water desalination
  - Brackish water TDS is similar to piranha wastewater TDS
  - Energy required to concentrate $10\frac{g}{l}$ sulfuric acid by a factor of 20:
    - ED $\approx 30\frac{kWh}{kgal}$, Distillation $\approx 800\frac{kWh}{kgal}$
  - ED has a small footprint
  - ED offers a degree of selectivity that distillation can not
  - ED safer than boiling acid
- Established electrodialysis equipment is easily modified for acid recovery
- Materials used to modify ED for acid recovery are now commercially available

Cons:

- Maintenance costs are significant, $\frac{\$40}{op\ hr}$
- ED is sensitive to oxidants and Piranha wastewaters contain the following oxidants:
    - Hydrogen peroxide (H_2O_2); Caro's Acid (H_2SO_5); Peroxodisulfuric Acid ($H_2S_2O_8$)

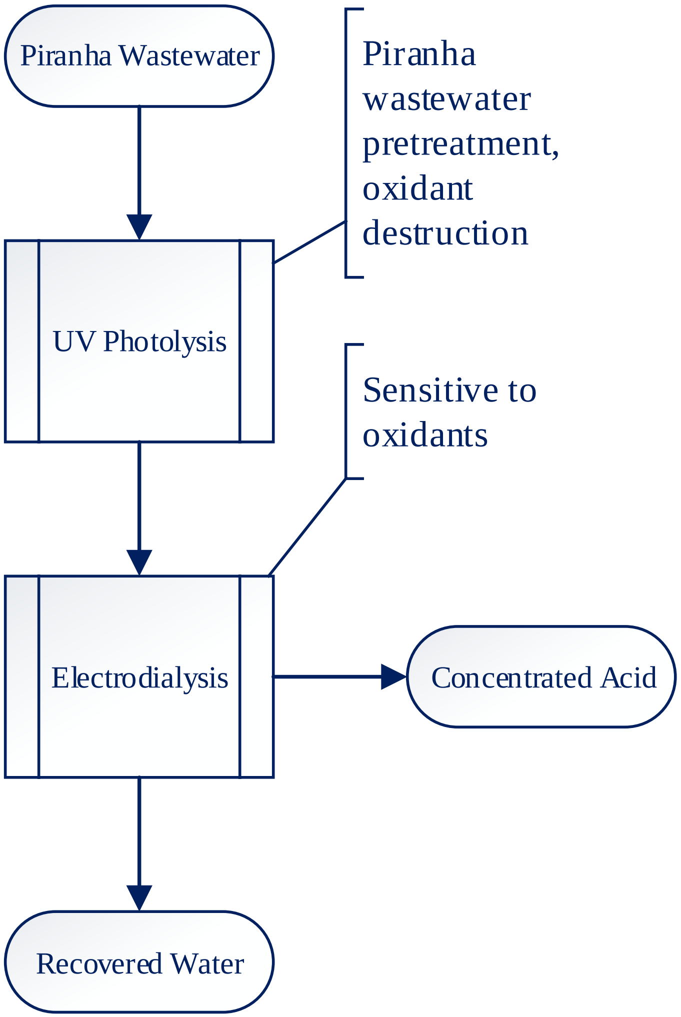
Acid & Water Recovery Block Flow Diagram

The process employs two unit operations:

1. UV Photolysis
   - Oxidant destruction
2. Electrodialysis (ED)
   - Water recovery
   - Concentrated acid production

Why UV Photolysis?

UV Photolysis can be implemented without neutralizing the sulfuric acid



UV Photolysis

UV photolysis reactors are normally used to sterilize water

It is known that UV photolysis can be used to accelerate oxidant decomposition

Research Goal:

Assess the use of UV photolysis to destroy oxidants in piranha wastewaters

These UV reactors are part of the San Francisco Public Utilities Commission's new Tesla Water Treatment Facility. It can treat 315 mgd.

Electrodialysis (ED)

Electrodialysis units consist of an anode and cathode with a stack of anion- and cation-exchange membranes sandwiched in between

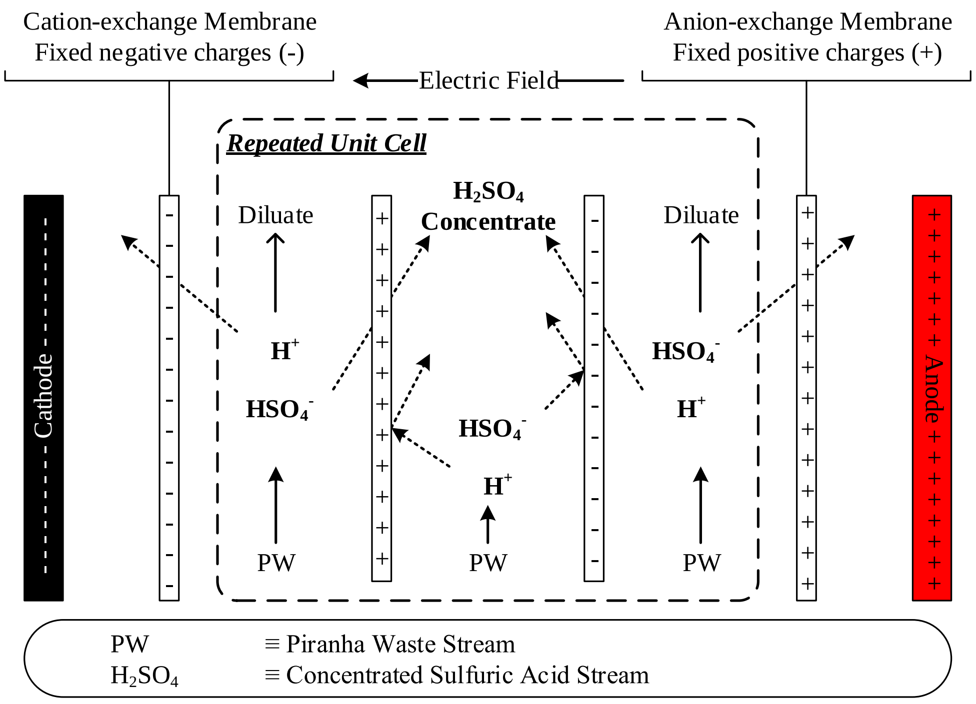
The anion- and cation-exchange membranes are arranged in an alternating pattern with a flow channel passing between each membrane pair

If an electric field is established between the anode and cathode, cations migrate toward the cathode and anions migrate toward the anode

Anions pass easily through the anion-exchange membrane, but are retained by the cation-exchange membrane

Cations pass easily through the cation-exchange membrane, but are retained by the anion-exchange membrane

This arrangement of membranes results in ion accumulation in every other compartment (**concentrate compartments**), and ion depletion in the remaining compartments (**diluate compartments**)



Schematic of electrodialysis (ED) unit

Electrodialysis Modification

Proton blocking anion-exchange membranes must be used to concentrate sulfuric acid

The anion-exchange membranes used for desalination can not adequately retain protons in the concentrate compartment

It has been shown that $10\%_{wt}$ sulfuric acid can be produced cost effectively with proton blocking membranes

Research Goal:

Assess water recovery and concentration of dilute sulfuric acid with various embodiments of electrodialysis

100 gpm ED system

Future Plans

Next-Year Plans:

- Characterize the chemistry of piranha generated wastewaters
- Assess water recovery and concentration of dilute sulfuric acid with various embodiments of electrodialysis
- Assess the use of UV photolysis to destroy oxidants in piranha wastewaters

Long-Term Plans:

- Identify optimal operating conditions for the modified electrodialysis stack
- Identify optimal operating conditions for the UV photolysis reactor
- Pilot scale testing of water and concentrated sulfuric acid recovery from piranha solutions and piranha generated wastewaters

Recognitions/Awards

Project Start Date 3-15-13

Jake Davis:

- Science Foundation Arizona Fellowship
- Arizona Water Sustainability Program Graduate Fellowship

Industrial Interactions and Acknowledgements

Industrial Interactions:

- Carl Geisert, FSM Sr. Principal Engineer, Intel Corporation
- Gopal Rao, FSM Research, Intel Corporation
- Varinder Malik, Water/Waste System Engineer, Intel Corporation
- Vicki Gruwell, Water/Waste System Engineer, Intel Corporation

Acknowledgements:

- Farhang Shadman, Chemical and Environmental Engineering, UA