Copper Recovery & Nanoparticle Removal from CMP Waste Water

(*Based on Previous Custom Project)*

PIs:

- **James Farrell, Chemical and Environmental Engineering, UA**
- **James C. Baygents, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Jake Davis, PhD candidate, Chemical and Environmental Engineering, UA**
- **David Hubler, PhD candidate, Chemical and Environmental Engineering, UA**

Undergraduate Students:

- **Melody Hendricks, Chemical and Environmental Engineering, UA**
- **Dave Niselson, Chemical and Environmental Engineering, UA**
- **George Chac, Chemical and Environmental Engineering, UA**

Cost Share (other than core ERC funding):

- **Intel Funding ($60k)**
- **University of Arizona Funding ($37.5k)**
- **Science Foundation Arizona Fellowship (Jake Davis, $46k)**
- **GEP Smith Fellowship & the Triffet Prize (David Hubler, $44k)**

Objectives

- Validate a novel integrated CMP waste water treatment & reclamation process, building on results from a previous custom project, for:
  - removal of silica nanoparticle from CMP waste water
  - recovery of copper from CMP waste water
  - reclamation of CMP waste water for reuse as fab feed supply
- Develop best operating conditions for integrated process units
- Pilot test integrated process for CMP waste water treatment & reclamation
- Develop clean & cost effective technology for point of use acid (pH~1.5) & base (pH~12.5) generation using electrochemistry

ITRS ESH Metrics

ITRS ESH Chemicals and Materials Management Technology Requirements—Near-term Years

- ***Nanomaterials (Critical)*: Conduct risk assessment by 2012-2017**
- ***Copper (Important)*: 95% of copper recovered by 2014-2017**

ITRS ESH Process and Equipment Management Technology Requirements—Near-term Years

- ***Chemicals (Important)*: Maintain or improve chemical utilization*; characterize process emissions & byproducts; improve PCU by 10% by 2012-2017**
- ***Water and other utilities (Important)*: Optimize consumption. Reduce water and utilities requirements**

ITRS ESH Facilities Technology Requirements—Near-term Years

- ***UPW recycled/reclaimed (% of 2007 use) (Important)*: 60% by 2016-2017**

ITRS ESH Impact

ITRS ESH Chemicals and Materials Management Technology Requirements—Near-term Years

- ***Nanomaterials*: Eliminate the emission of silica nanoparticles in CMP waste water**
- ***Copper*: Recover copper from CMP waste water**

ITRS ESH Process & Equipment Management Technology Requirements—Near-term Years

- ***Chemicals*: Reduce strong acid use for primary IX regen. by 79%**

[Savings of $0.213 per kgal treated (acid only, $0.15 per liter of 38% HCl, assume 50ppm $CaCO_3$ in FCB effluent)]

- ***Chemicals*: Reduction in emission of primary ion exchange regeneration brines by 79%**
- ***Water and other utilities*: Reduction in the amount of water used for regeneration of primary ion exchange resin by 79%**

ITRS ESH Facilities Technology Requirements—Near-term Years

- ***UPW recycled/reclaimed*: Reduction in the use of potable water by reclaiming 98% of CMP waste water (*CMP accounts for ~30% of the water used during IC fabrication*)**

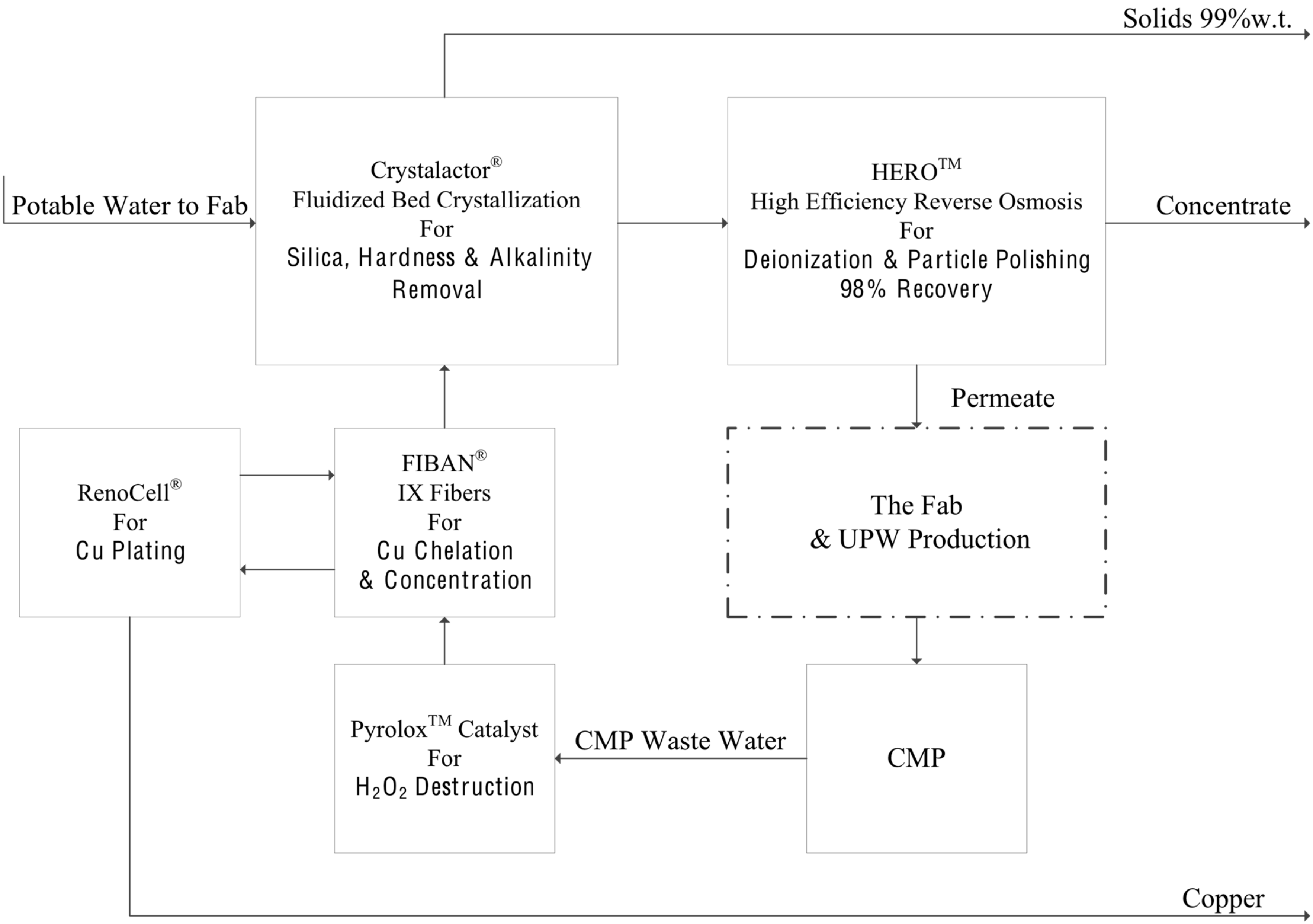
Key & Distinguishing Features

1) *Cost effective copper recovery using RenoCell® technology*

2) *Novel use of Pyrolox™ technology as a catalyst for H_2O_2 destruction*

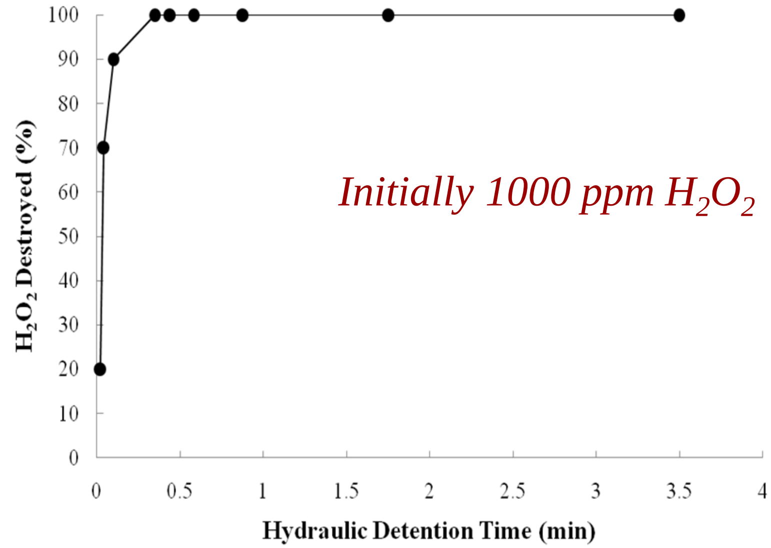
3) *Exploitation of new FIBAN® fibrous ion exchange technology to eliminate the need for expensive filtration or off-site regeneration of IX resin*

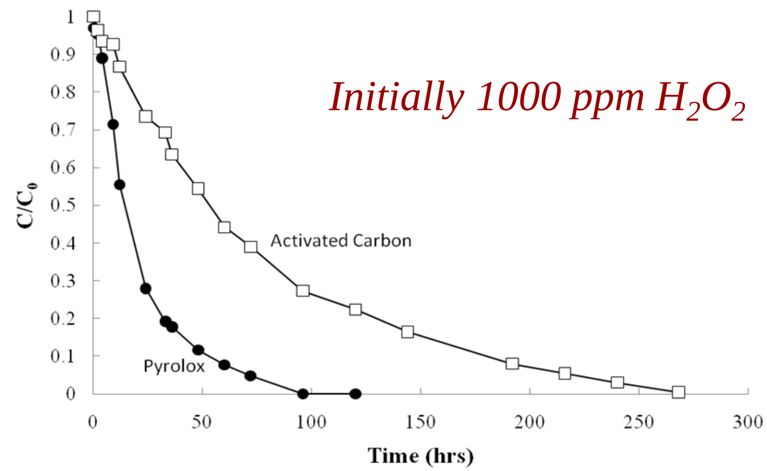
1) *Application of Crystalactor® & HERO™ technology to CMP waste water to:*
   - *Eliminate silica nanoparticles*
   - *Eliminate chelating agents & corrosion inhibitors*
   - *Eliminate UPW primary ion exchange for control of:*
     - *Hardness*
     - *Alkalinity*
   - *Reclamation of CMP waste water for fab feed water*


Solids 99%w.t.
Potable Water to Fab
Crystalactor®
Fluidized Bed Crystallization
For
Silica, Hardness & Alkalinity
Removal
HERO™
High Efficiency Reverse Osmosis
For
Deionization & Particle Polishing
98% Recovery
Concentrate
Permeate
RenoCell®
For
Cu Plating
FIBAN®
IX Fibers
For
Cu Chelation
& Concentration
The Fab
& UPW Production
Pyrolox™ Catalyst
For
H_2O_2 Destruction
CMP Waste Water
CMP
Copper

Catalytic Degradation of H_2O_2 with Pyrolox™

- Pyrolox™ (MnO_2) is granular media commonly used in water treatment
- Pyrolox™ has proven an effective catalyst for hydrogen peroxide destruction
- Pyrolox™ is better than GAC
  - ✓ Pyrolox™ is not fouled by chelators
  - ✓ Pyrolox™ has faster kinetics
  - ✓ Does not degrade

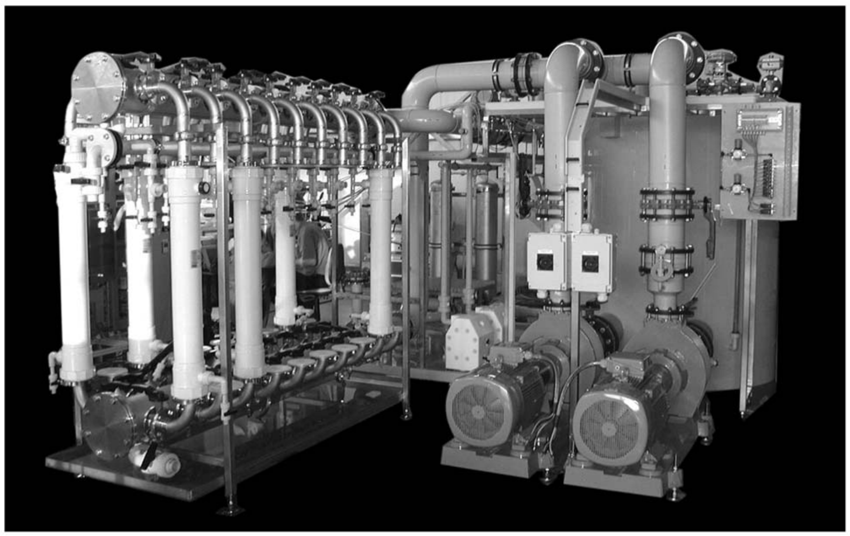




Current Copper Recovery Technologies

Pall Microza[1] Filtration

Actual Capital Cost Data:$1.5 – $2.5 Million
Actual CoO Data:$1.90-$3.10 per kgal treated
(excl. Capital & Labor Costs)



Siemens Copper Select™

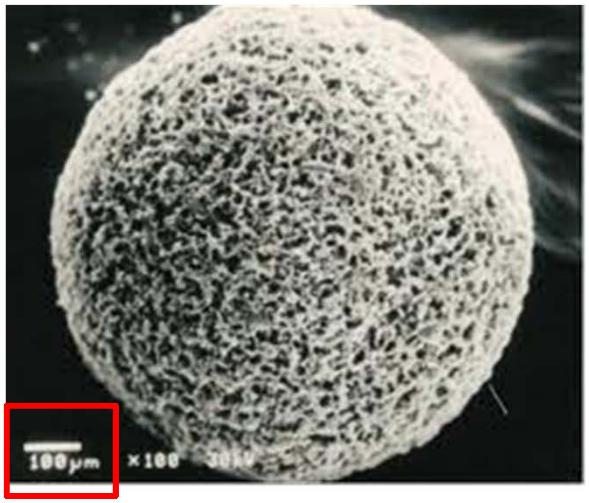
Requires transport of copper laden ion exchange resin ***off site*** *for regeneration*

[1] Microza is a trademark of Asahi Kasei Corporation

FIBAN® Fibrous Ion Exchange Technology

about 0.65 mm

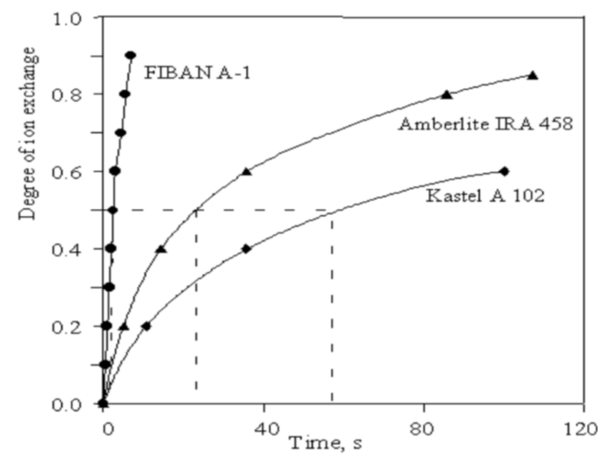
Porous IX Bead



- *Most IX sites in IX bead interior*
- *Silica nanoparticles dissolve and foul bead during normal regeneration*
- *IX beads require* ***off-site*** *regeneration*

FIBAN® Filaments

- ✓ *Most IX sites on FIBAN® surface*
- ✓ *FIBAN® can be regenerated at pH~1.5*
- ✓ *FIBAN® can be regenerated* ***on-site***



Copper Recovery *with* RenoCell® Technology

***Regeneration** of 1 m^3 of 50 mg-Cu per g-resin*
***Recover** $320 of copper ($4/lb)*
***Costs** $8.40 ($0.10/kWh)*

RenoCell®

Electroplating copper
with
zero acid consumption

Acid generation at anode
Cu deposition on cathode

Throwaway carbon felt cathode (left)

Copper laden carbon felt cathode from bench reactor (right)

Fluidized Bed Crystallization *with Proven* DHV Crystalactor® Technology

FCB is common practice in the Netherlands WTP (Waternet) since the late 1980s

The fluidized bed reactor is partly filled with seeding material (dia. 0.2-0.4 mm, garnet)

The seeding material in a fluidized condition

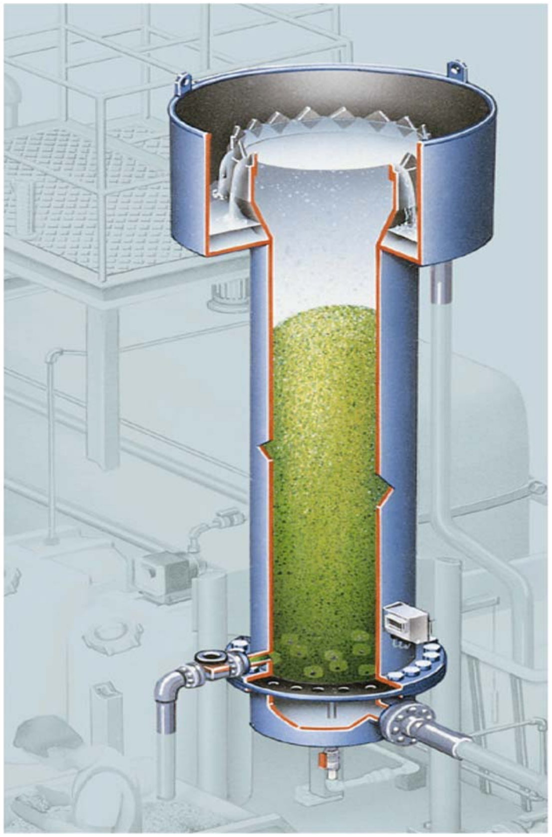
In the bottom of the reactor, chemicals are dosed (caustic soda, soda ash or lime)

Carbonate & hydroxide minerals rapidly crystallize on the seeding material forming pellets

Pellets are removed from reactor bottom & can be re-used in industry

Dry bottom product, solids content of around 99%w.t.

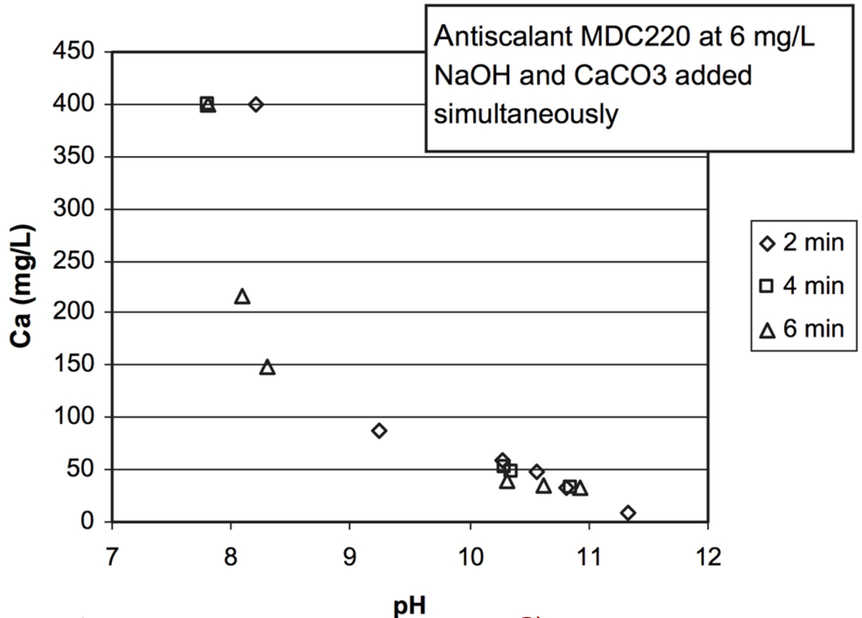
DHV Crystalactor®

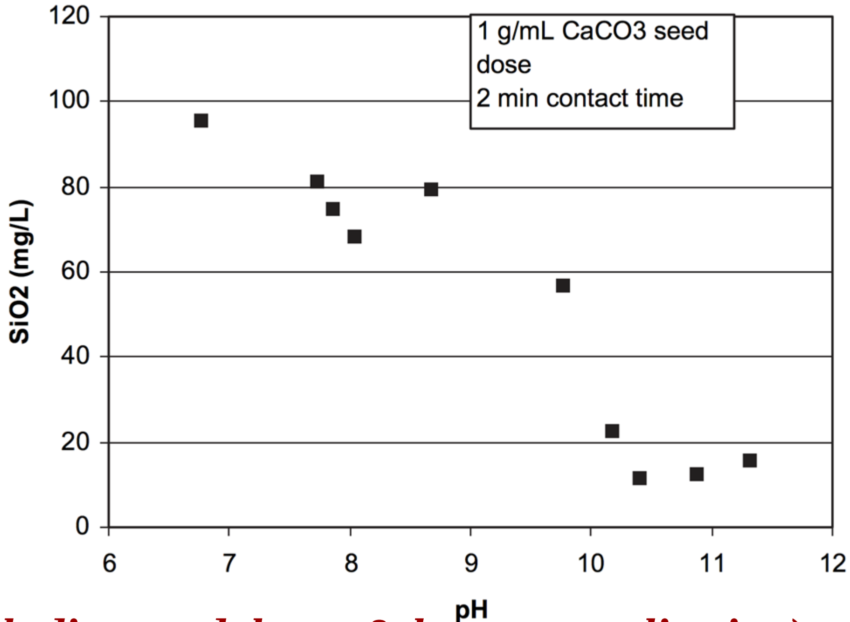


Dijk, J.C. and Wilms, D.A., Water treatment without waste material-fundamentals and state of the art of pellet softening, J Water SRT-Aqua,1991, 40, 263-280

Fluidized Bed Crystallization **Investigation Funded By:**

City of Phoenix Water Services Department; California Energy Commission; AWWA Research Foundation;





$0.049 per kgal treated*[3)] – FCB cost *(including seed, base, & base neutralization)

***$0.213 per kgal treated* – IX regeneration costs avoided with FCB**

(acid only, $0.15 per liter of 38%w.t. HCl, assuming 50ppm $CaCO_3$ in FCB effluent)

1) Snyder, S.A., Inland Desalination: Current Practices, Environmental Implications, & Case Studies in Las Vegas, NV, Sustain. Sci. and Eng., 2010, 2, 327-350
2) Bond, R. and Veerapaneni, S.V., Zero Liquid Discharge for Inland Deslaination, AWWA, 2007
3) van Schagen, K., Rietveld, L., Babuska, R., Baars, E., Control of the fluidised bed in the pellet softening process, Chem. Eng. Science, 2008, 63, 1390-1400

HERO® High **E**fficiency **R**everse **O**smosis

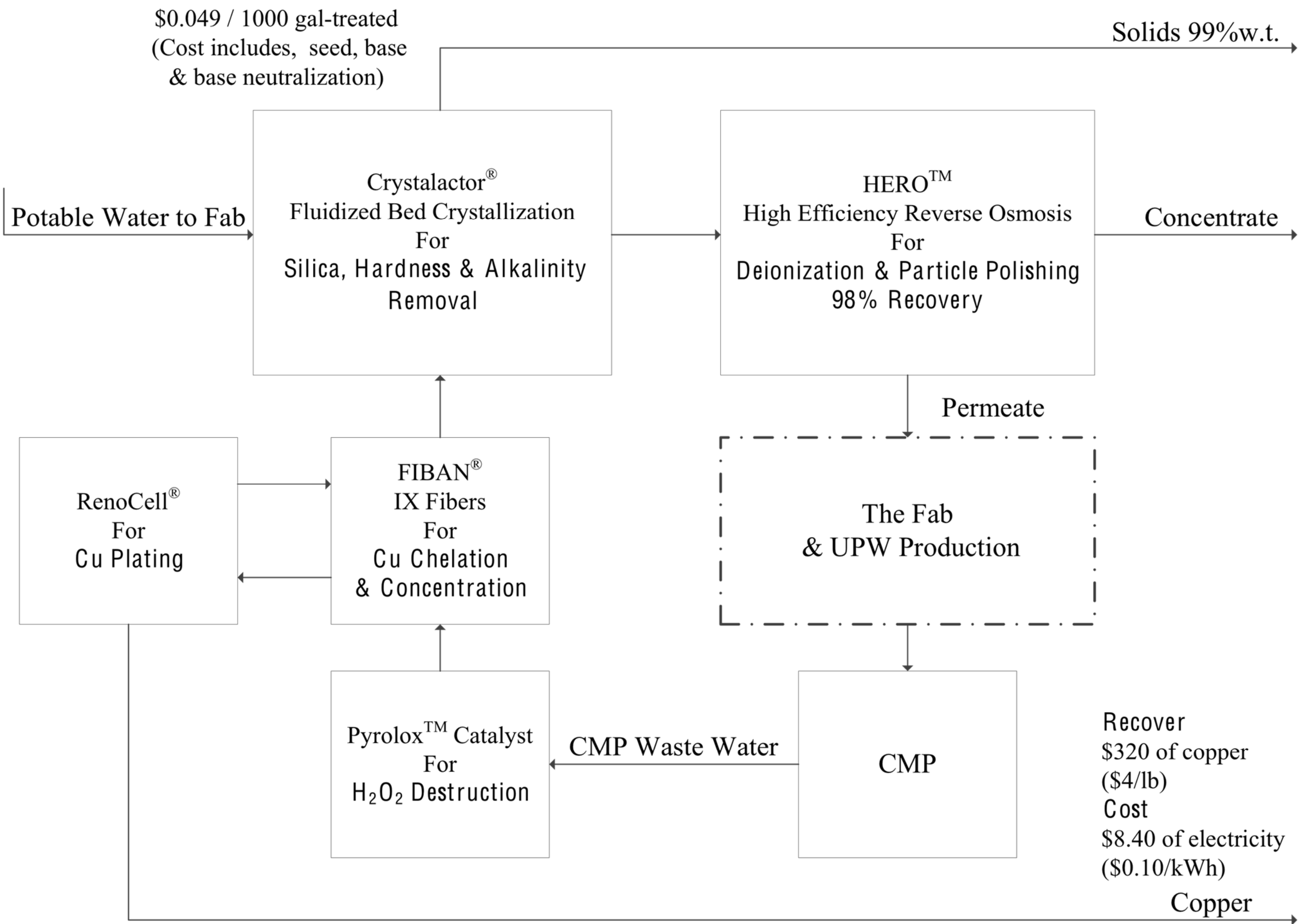
HERO® is a technology employed in semiconductor manufacture

HERO® units are fed pH ~ 9 water
Base accumulates on the concentrate side of the RO membrane
Concentrate effluent pH ~ 11

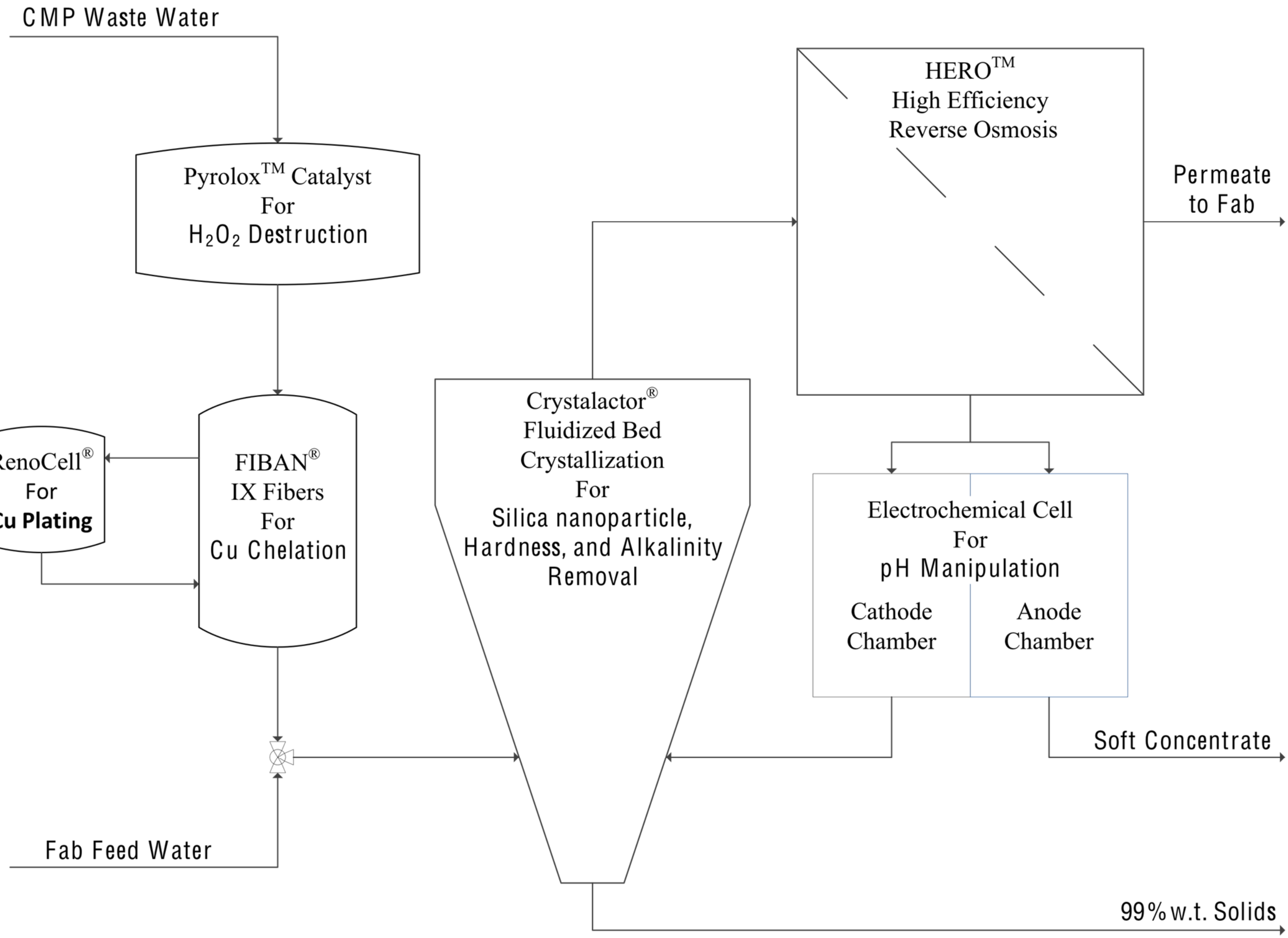
The membrane and membrane foulants are
negatively charged at pH > 9

Waters with silica concentrations in excess of 1000 ppm are effectively treated with HERO®

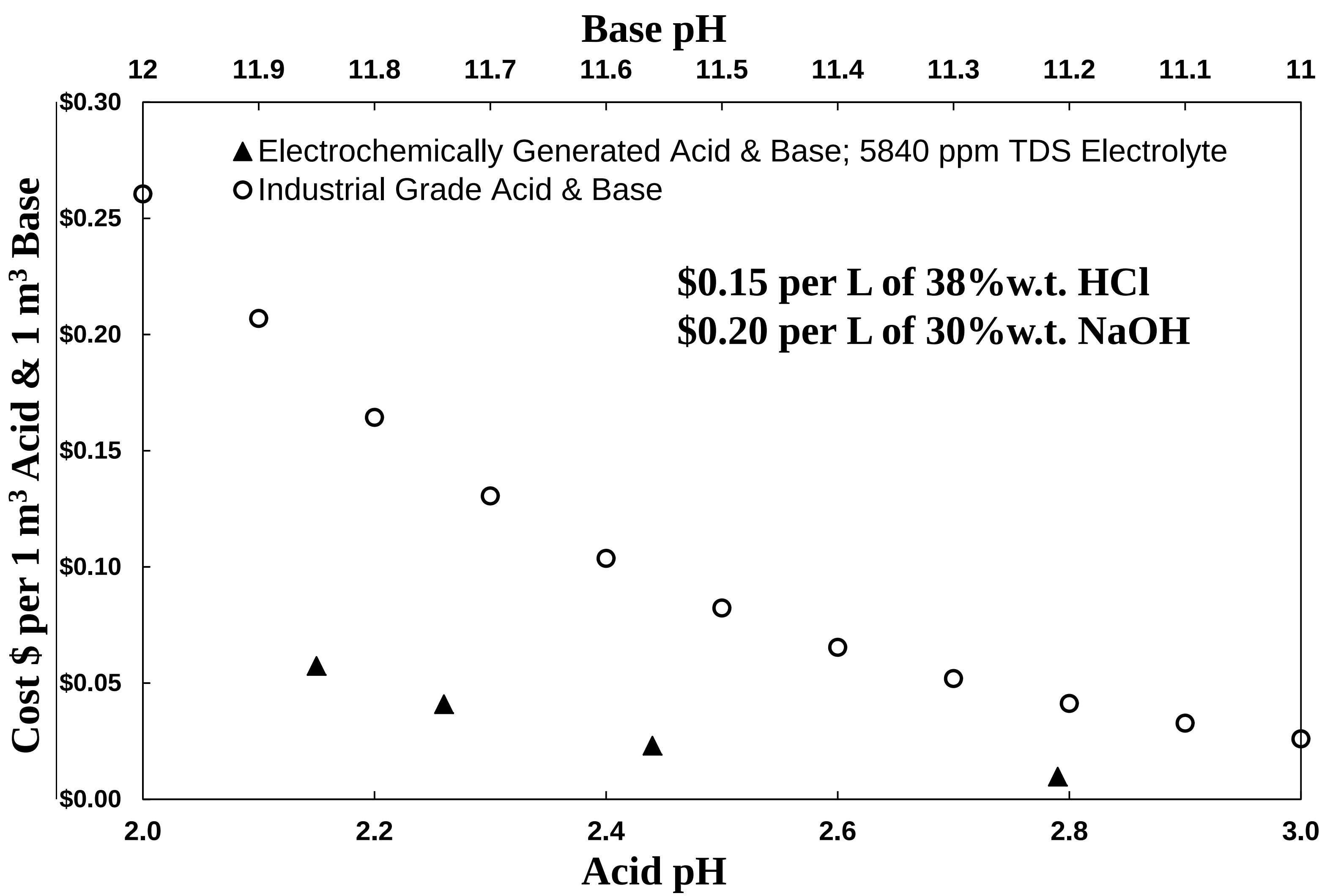
HERO® water recoveries in excess of 98%



SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing


CMP Waste Water
Pyrolox™ Catalyst For H_2O_2 Destruction
RenoCell® For Cu Plating
FIBAN® IX Fibers For Cu Chelation
Fab Feed Water
Crystalactor® Fluidized Bed Crystallization For Silica nanoparticle, Hardness, and Alkalinity Removal
HERO™ High Efficiency Reverse Osmosis
Permeate to Fab
Electrochemical Cell For pH Manipulation
Cathode Chamber
Anode Chamber
Soft Concentrate
99% w.t. Solids

Electrochemical Acid & Base Generation



Intel Contacts & Collaborators

- **Dan Dodges** *dan.hodges@intel.com*
- **Don Hooper** *don.fab11.hooper@intel.com*
- **Allen Boyce** *allen.r.boyce@intel.com*

Future Plans

Next Year Plans

- **Funding ended 4/1/10**

Long-Term Plans

- **Seek partners for proposal**

Publications, Presentations, and Recognitions/Awards

- David Hubler: Triffet Prize and GEP Smith Fellowship;
  First Place Award, University of Arizona 2009 Student Showcase, B.P.A. Division, November 6-7, 2009, Tucson, AZ
- Jake Davis: Science Foundation Arizona Fellowship, NASA Space Grant
- "Economic Benefit of Commercial and Industrial Water Uses in a Semi-arid Municipality," presented at the Arizona Hydrological Society/American Institute of Hydrology 2009 Hydrological Symposium, August 30-September 2, 2009, Scottsdale, AZ
- "Electrochemical Methods for Water Reclaim in Semiconductor Manufacturing," presented at the International Conference on Microelectronics Pure Water, November 11-12, 2008, Mesa, AZ
- "Electrochemical Water Treatment using Diamond Film Electrodes," presented at the University of Illinois at Urbana-Champaign, November 7, 2008
- "Evaluating Economic Impacts of Semiconductor Manufacturing in Water-Limited Regions," submitted to *Journal of the American Water Works Association*
- "Reclamation of Copper-CMP Wastewater," presented at the International Conference on Microelectronics Pure Water, November 16-17, 2010, Mesa, AZ