Key Issues Affecting Water Use & Recycle in HVSM

Teleseminar By: Jake Davis, PhD Candidate (jrdavis@email.arizona.edu)

Teleseminar Date: May 19th, 2011

Outline

- Concerns about public water supplies
  - *Future availability of water resources*
  - *Future quality of water resources*
- Challenges affecting the semiconductor industry
  - *Acquisition of water resources needed for semiconductor manufacturing industry growth*
  - *Minimize the industries liability for utilizing materials with poorly characterized environmental and health characteristics*
  - *Develop strategies to meet future waste disposal requirements*
- Technologies which we are currently investigating that address these concerns and challenges
  - *Replacement of conventional ion exchange materials*
  - *POU generation of dilute acid and base from RO concentrate*
  - *A combined water softening and fluoride treatment process*
  - *CMP wastewater recycle with currently available treatment technologies*

Future Availability of Water Resources

Water supplies are being increasingly challenged by:

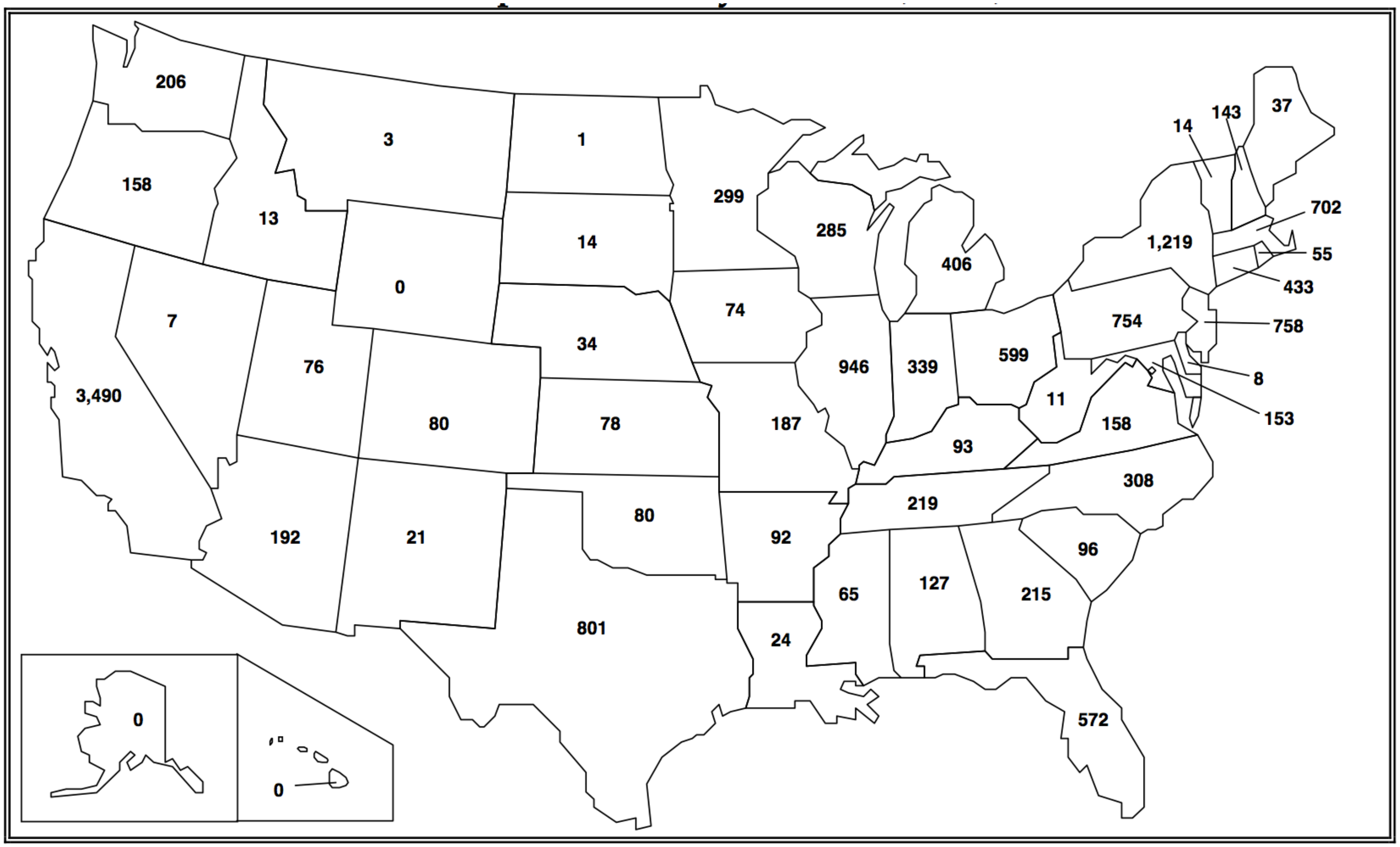
- extended droughts
- water demand growth due to population increase
- more stringent health-based regulations, and
- competing demands from a variety of users

Some Quick Facts[1]

- Assuming continued per capita water use, 16 trillion additional gallons per year will be used in the U.S. by 2020. This is equivalent to ¼ of the combined outflow from ALL of the Great Lakes.
- In CA, demands already exceed supplies by 326 billion gallons per year.
- 50% of the growth in the U.S. is forecasted to occur in CA, TX, and FL — regions already experiencing water shortages.

[1]Desalination and Water Purification Technology Roadmap, 2003

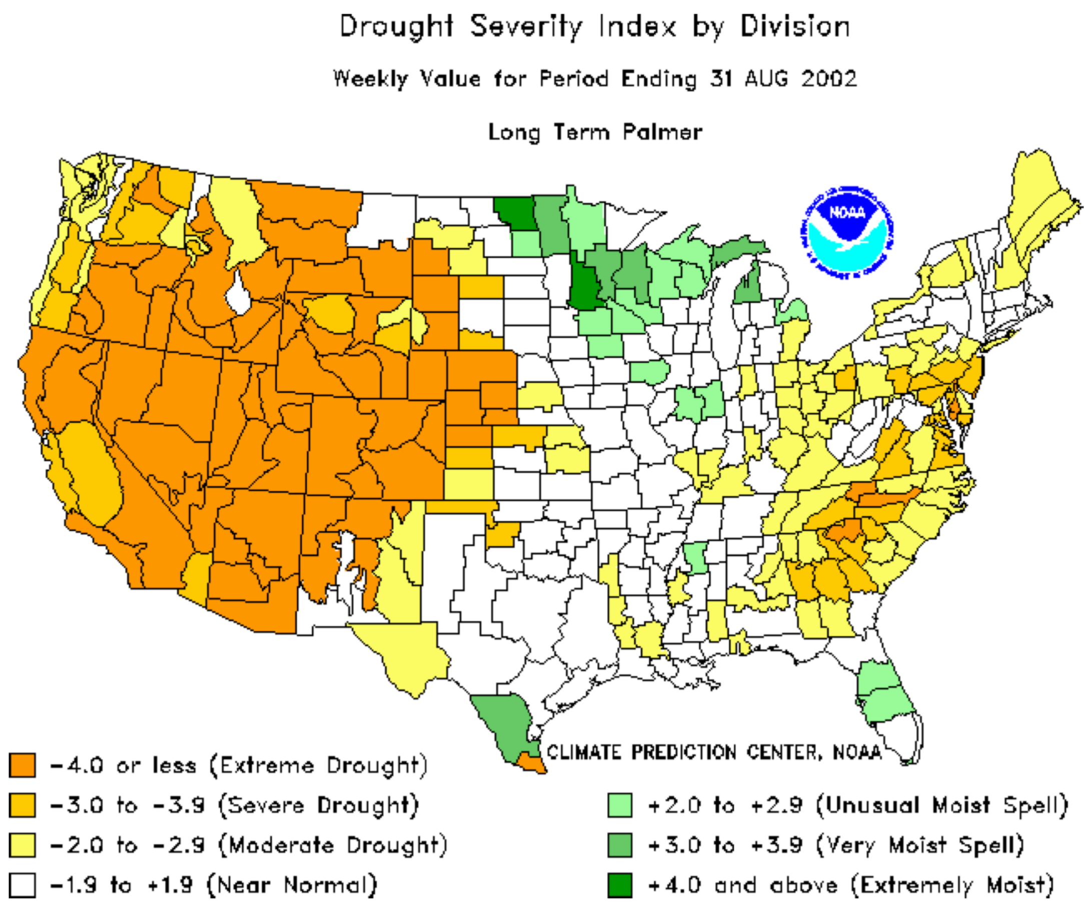
Geographic Distribution of and Number of Companies in the Electronics/Computer Industry*



Source: Based on 1992 Bureau of the Census data.

*USEPA Office of Compliance Sector Notebook Project, Electronics and Computer Industry,1995

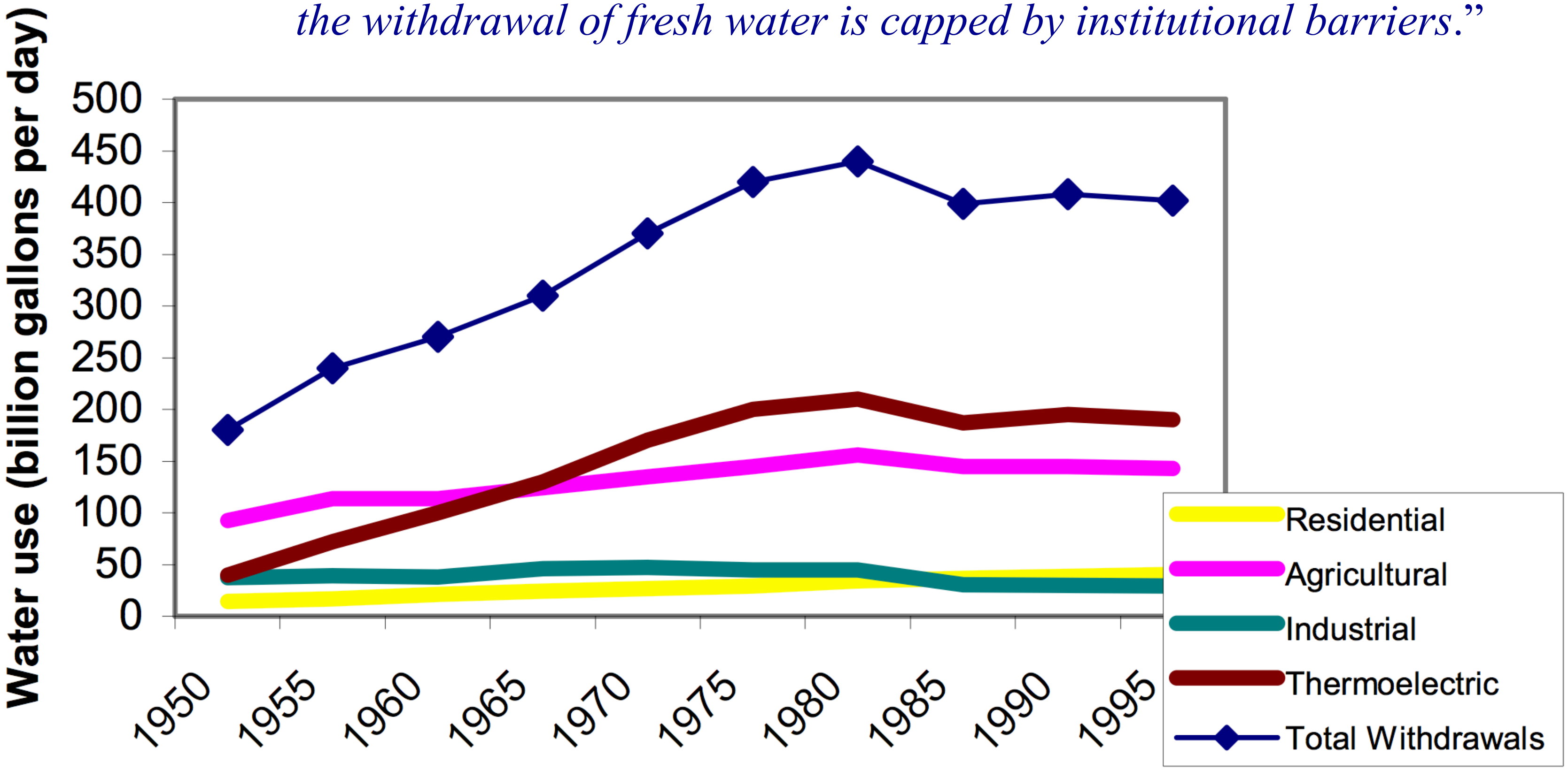
Drought in the U.S.



Desalination and Water Purification Technology Roadmap, 2003

Water Resource Limitations

"The cause of the plateau in the water use is singular:
the withdrawal of fresh water is capped by institutional barriers."

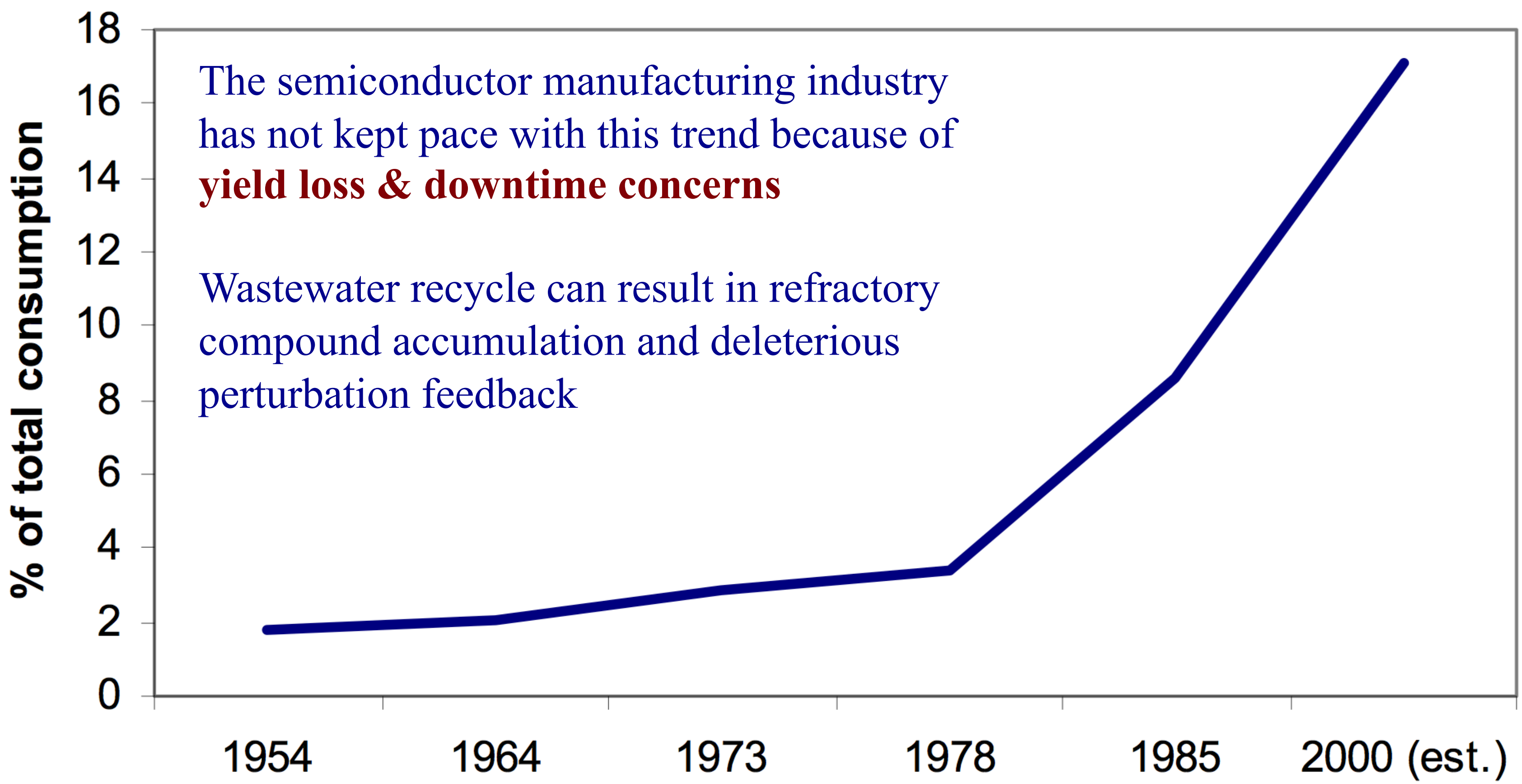


Desalination and Water Purification Technology Roadmap, 2003

Industrial Water Recycling Rate in the U.S.

The semiconductor manufacturing industry has not kept pace with this trend because of **yield loss & downtime concerns**

Wastewater recycle can result in refractory compound accumulation and deleterious perturbation feedback



Desalination and Water Purification Technology Roadmap, 2003

The Semiconductor Industry Can Currently Afford Not to Recycle

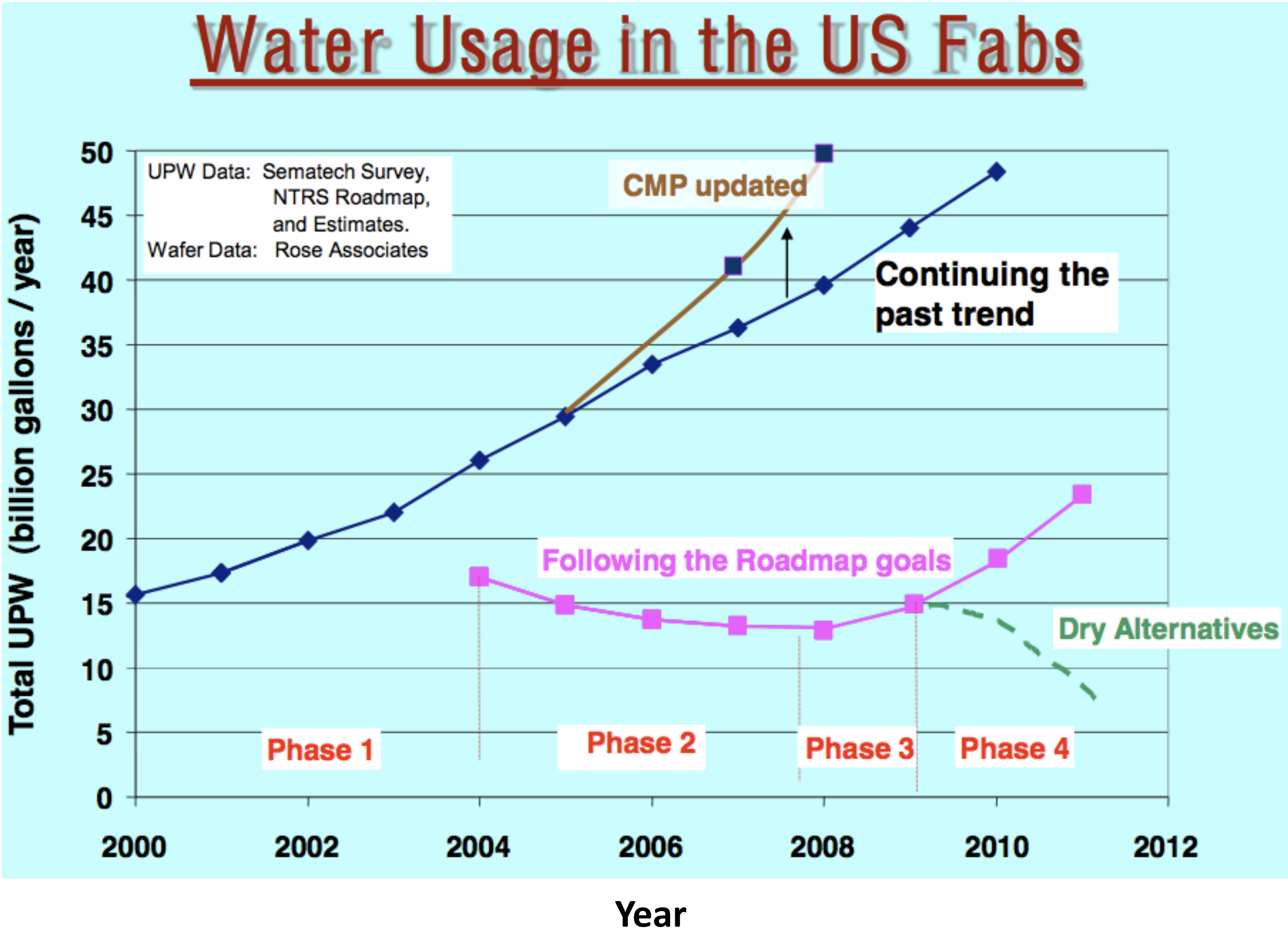
Treatment cost for fresh water from a conventional water treatment plant	$0.30-0.40/1000 gallons
Reclaimed water for industry in Southern California	$2.22/1000 gallons
Treatment cost for desalinated brackish water for residential use	$1-3/1000 gallons
Treatment cost desalinated seawater	
Santa Barbara, CA (1992)	$5.50/1000 gallons
Cyprus-2 (1999)	$3/1000 gallons
Tampa Bay (2001)	$2.08/1000 gallons

Desalination and Water Purification Technology Roadmap, 2003

Company	Revenues	Primary products
Intel	$20,870,000,000	Microprocessors
National Semiconductor	$ 2,623,100,000	System level products for fax machines, local and wide-area networking and telecommunications
Advanced Micro Devices	$ 1,953,019,000	Microprocessors
Cypress Semiconductor	$ 528,400,000	Memory chips and programmable logic devices
Cyrix	$ 183,825,000	Microprocessors
SEEQ Technology	$ 31,338,000	Local Area Network (LAN) chips

Source: U.S. Securities and Exchange Commission (SEC). 1997. Edgar database 10K Reports. Washington, D.C.: Government Printing Office. Available at http://www.sec.gov/cgi-bin/srch-edgar?

Mazurek, J., 2000 How fabulous fablessness? Environmental challenges of economic restructuring in the semiconductor industry. Greener Management International



Slide courtesy Dr. Farhang Shadman

HVSM & Water in the Future

In the future, the semiconductor industry will be forced to used poorer quality waters.

The semiconductor industry needs technologies that will facilitate cost effective production of UWP from impaired water supplies.

&

The net water consumed per wafer must be reduced. Impending regulation will prevent the continued increases in gross water use of HVSM.

- Wastewater recycle appears to better than the alternative water consumption reduction options:
    - *process chemistry reformulation, and*
    - *tool redesign*

The Safety of Public Waters

Contamination of water supplies is the result of both human activities and natural processes.

Contaminant removal presents a moving target -- as understanding of contaminant effects improve, regulation governing the acceptable levels of those contaminants become increasingly strict.

Common Contaminants:

- Biologics
- Salts (TDS)
- Metals
- ‘Pharmaceutics’ (including caffeine and endocrine disruptors)

New Materials in HVSM & Safety of Public Water Supplies

The semiconductor manufacturing industry is on the cutting-edge of materials application. It is likely to employ materials with poorly characterized environmental and health characteristics.

- Historically: Fluorinated organics (*i.e.*, PFOS)
- Currently: Nanoparticles

Utilization of poorly characterized materials exposes the industry to liabilities:

- Legal action
- Impromptu regulation
  - *Processes redesign and retrofit*

The technologies developed for HVSM wastewater recycle provide the industry with tools needed to remove materials from the wastewater prior to discharge, allowing the industry to limit these liabilities.

The Safety of Public Waters & Concentrate Disposal

The technologies commonly used to upgrade the quality of waters produce large quantities of high TDS concentrate.

These concentrates are not always disposed of in a manner that prevents them from reentering the water cycle.

Finding cost and environmentally sensitive disposal options for these concentrates is difficult.

Common Concentrate Disposal Methods

Currently most concentrate flows are discharged to the sewer.

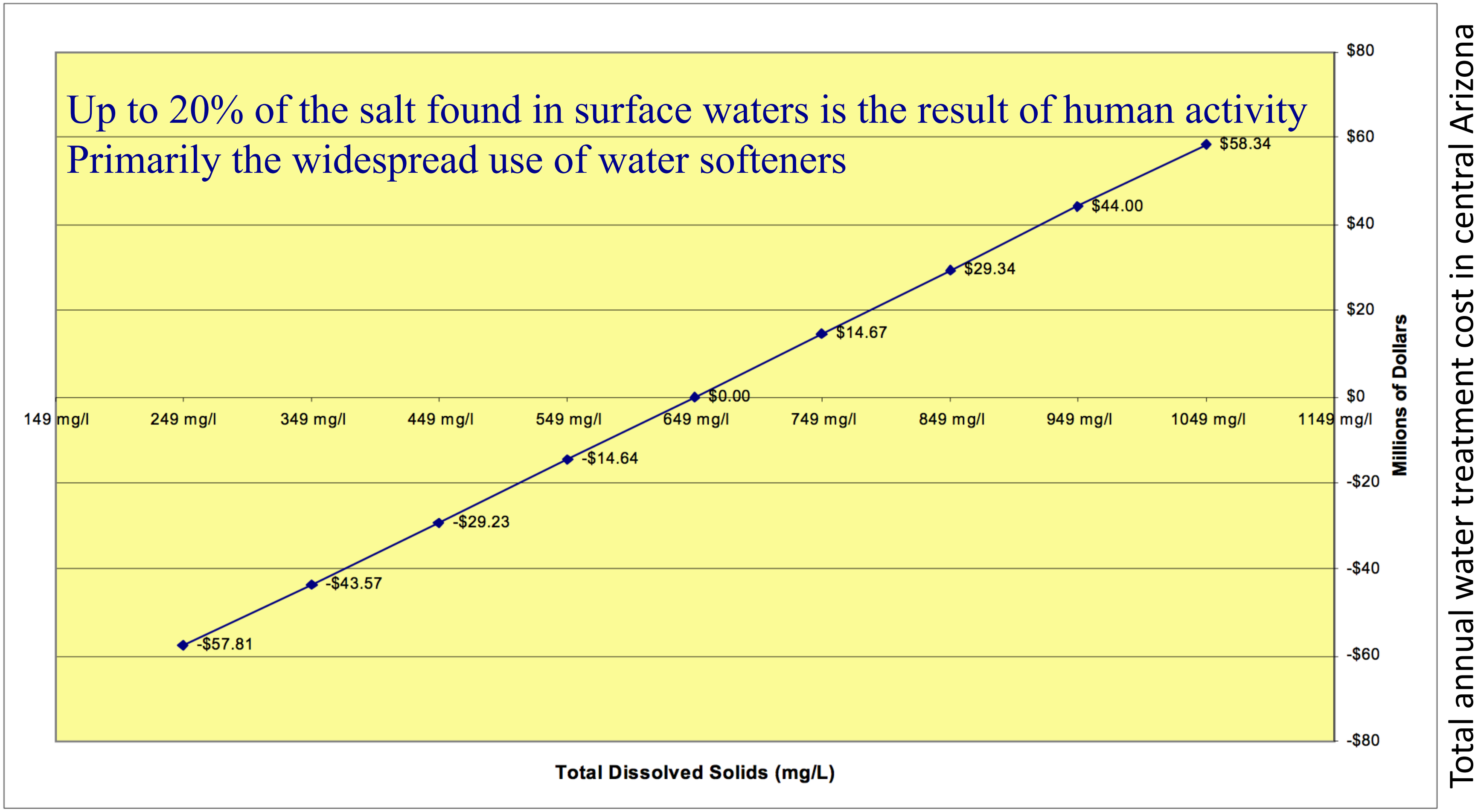
High TDS concentrates discharged to the sewer reenter the public water supply: deep well injection; release to surface waters.

It is not likely that metered discharge to the sewer will continue to be an acceptable concentrate disposal option.

Facility	Type of Water Treatment	Water Treatment Capacity (MGD)	Concentrate Disposal type	Comment
City of Chandler	RO	3	Sewer, and evaporation ponds	This facility treats Intel's waste water. The concentrate is then evaporated in ponds.
City of Scottsdale	RO	12	Sewer	Concentrate is discharged to sewer system, which ultimately ends up at the SROG 91st Avenue WWTP.
City of Gila Bend	RO	1.2	Evaporation Ponds	
Lewis Prison	RO	1.5	Evaporation Ponds	Due to inefficient treatment process, concentrate streams are greater than 15% which makes the ponds undersized
Town of Buckeye	Electrodialysis Reversal	0.9	Sewer	Treatment facility is old and only used for peaking purposes.
Yuma	RO	102	La Cienga By-Pass	Concentrate discharged to the Gulf of California. Plant has not operated since 1993.
City of Goodyear	RO	1.5	Sewer	
Industrial Users	RO	Varies	Sewer	Hospitals, bottling industry and microchip industry utilize treated water in their daily operations.

Central Arizona Salinity Study, 2003

Annual Costs Due to Changes in Salinity of CAP Water



Central Arizona Salinity Study, 2003

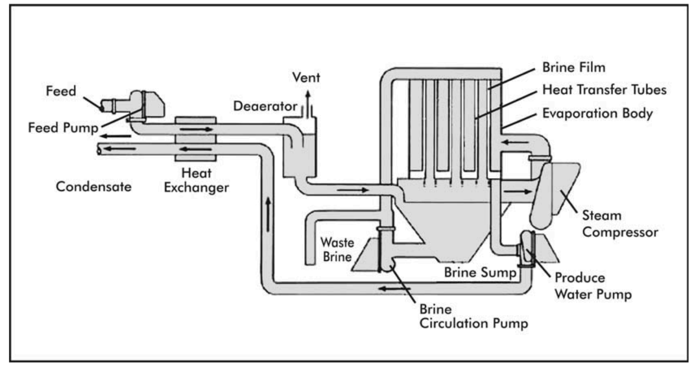
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
Teleseminar By: Jake Davis, PhD Candidate, University of Arizona

Zero Liquid Discharge (ZLD)

The increasing costs associated with treating high TDS waters are driving municipalities to mandate ZLD.

- New Mexico

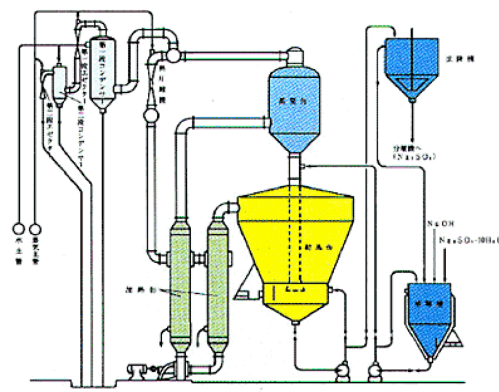
Brine Concentrator Schematic



This will drastically increase the cost of wastewater treatment:

- Brine concentration
- Crystallization
- Evaporation Ponds
- Solids Handling

Crystallizer Schematic



Central Arizona Salinity Study, 2003

Concentrates & HVSM

HVSM generates large volumes of high TDS concentrate:

- Regeneration of ion exchange softening systems
  - *A single regeneration cycle can produce anywhere from 80 to 320 kg of concentrate per cubic meter of ion exchange media*
- Reverse Osmosis
  - *The concentrate flow from RO units is 10-20% of the feed flow (potable water)*

Impending concentrate discharge regulation (*e.g.*, ZLD, *etc.*) will have a significant impact on the semiconductor industry.

Wastewater recycle will reduce concentrate flows:

- HVSM wastewater is soft – No ion exchange softening brine
- HVSM wastewater has low TDS – Small RO concentrate flow

Technologies which we are currently investigating that address public concerns and semiconductor industry challenges

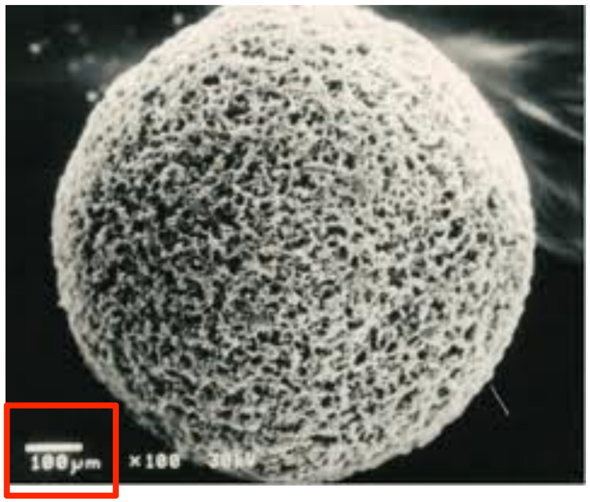
- Replacement of conventional ion exchange materials
- POU acid and base generation from RO concentrate
- A combined water softening and fluoride treatment process
- CMP wastewater recycle

Elimination of conventional ion exchange materials

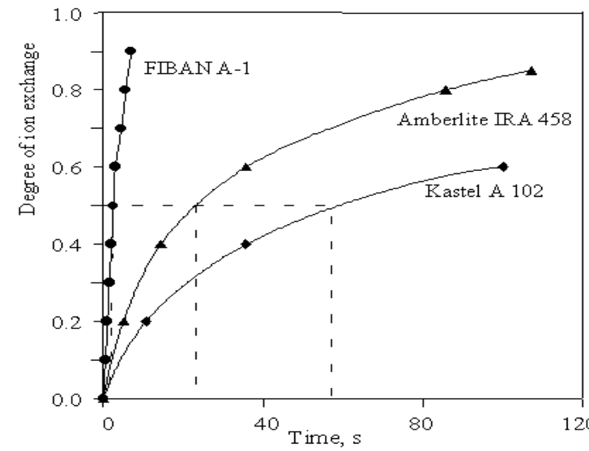
Softening *with* FIBAN® IX Fibers

about 0.65 mm

Porous IX Bead



- ○*Most IX sites in IX bead interior -- poor mass transfer characteristics*
- ○*IX beads require regeneration with concentrated acids – pH~ (-1) - 0*
- ○*Regeneration with concentrated acids produce concentrates*

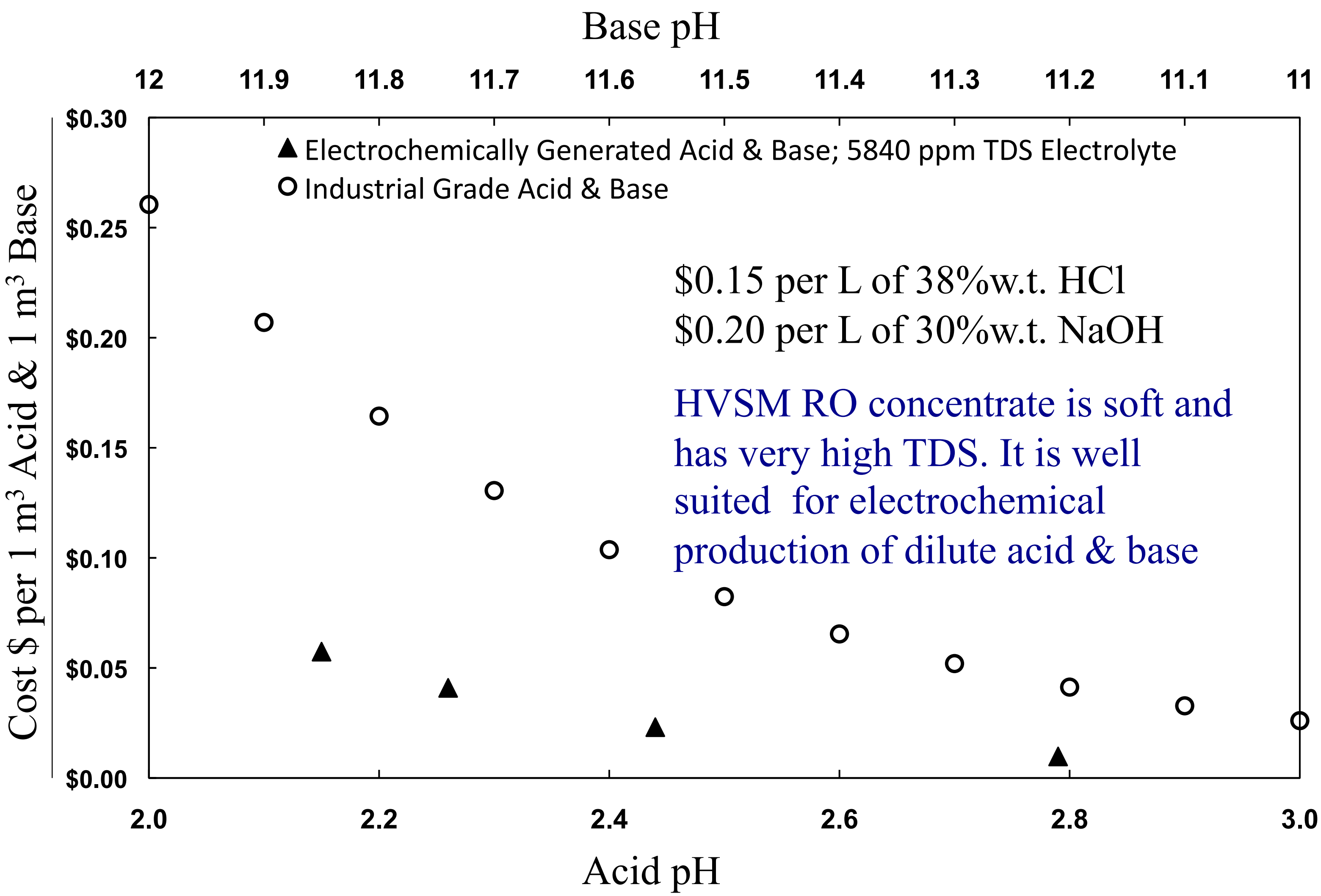


FIBAN® Filaments

- ✓*Most IX sites on FIBAN® surface – good mass transfer*
- ✓*FIBAN® can be regenerated at pH~2.5-1.5 (Softening)*
- ✓*Regeneration of FIBAN® will produce less concentrate*

POU acid & base generation

Electrochemical Acid & Base Generation



A combined water softening and fluoride treatment processes

Current Fluoride Treatment Process

Treatment of fluoride containing wastewater is most commonly accomplished in two steps:

1) reduction of the fluoride concentration to approximately 10ppm by calcium fluoride ($CaF_{2(s)}$) precipitation
   - *Coagulation with calcium chloride*
   - *Flocculation*
   - *Settling*
   - *Filtration*
   - *Disposal of valueless sludge ($100 per 1000 gal of sludge disposed)*

2) further reduction of the fluoride concentration to the MCL of 4ppm by sorption with activated alumina
   - *Activated alumina must be periodically regenerated with concentrated base*

The Combined Water Softening & Fluoride Treatment Process

Two part process:

1. Soften the feed water by fluidized bed crystallization resulting in the production of dry calcite pellets (dia. 1.5mm)
   - *Reactor feed pH ~ 9.5*

2. Fluoride containing waste waters are fed through a column containing calcite pellets resulting in the production of chemical grade fluorspar pellets (value: $500/ton)
   - *Reactor feed pH~ 6.5*

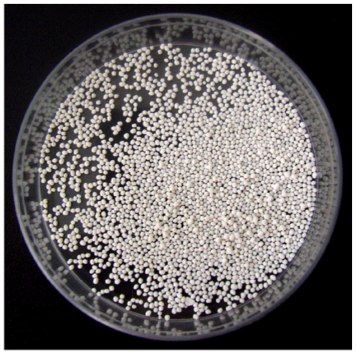
- All pH manipulations can be accomplished with the electrochemical cell

Advantages

- No IX regeneration concentrate
- No activated alumina regeneration concentrate
- No Sludge disposal
- Easily handled solids
- $500 of value added per ton of pellets produced
- Only two pieces of equipment not six
- Columns have no moving parts

Calcite Pellets

CaF_2 Pellets



Discharged Pellets

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

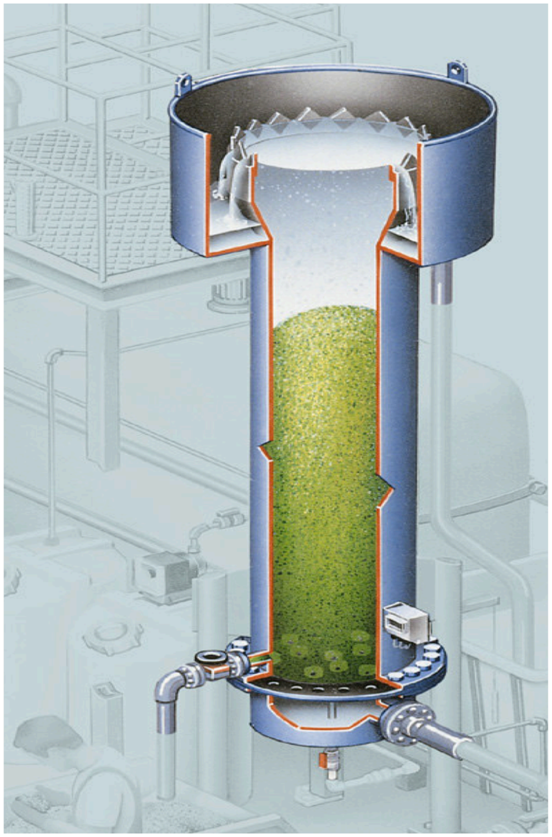
Fluid velocity ~ 2.5 m/min

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

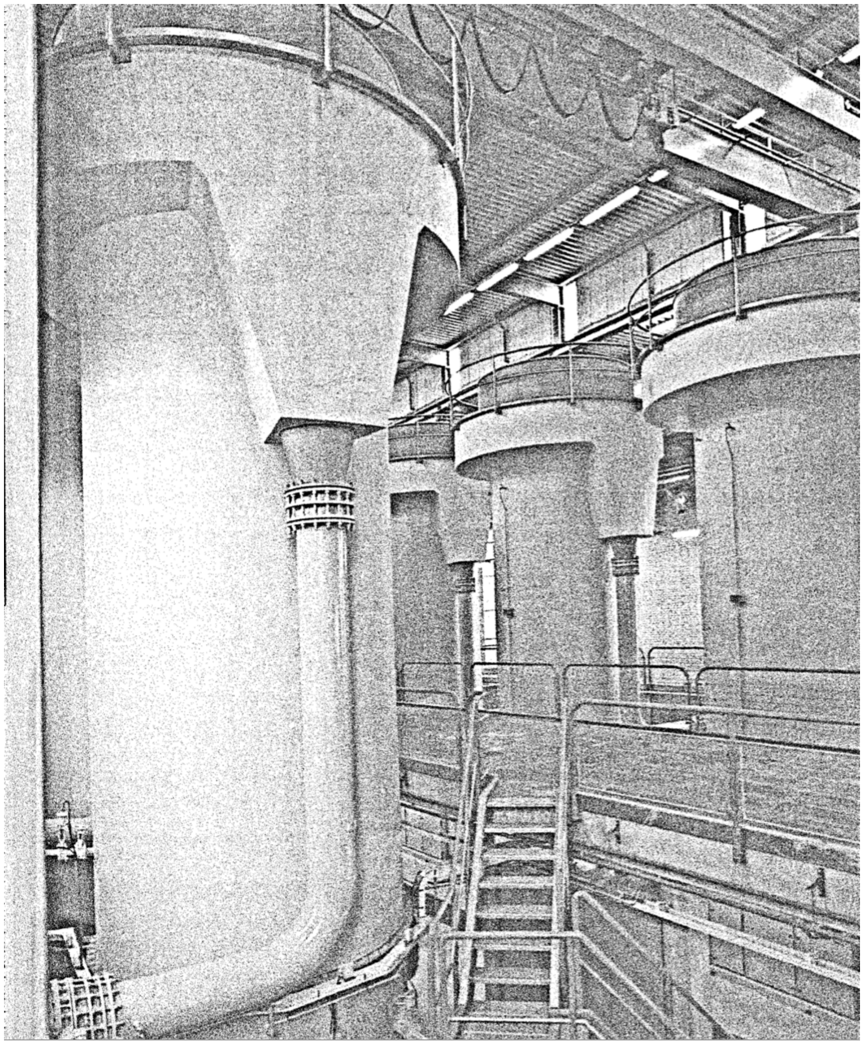
Dry bottom product, solids content of around 99%w.t.

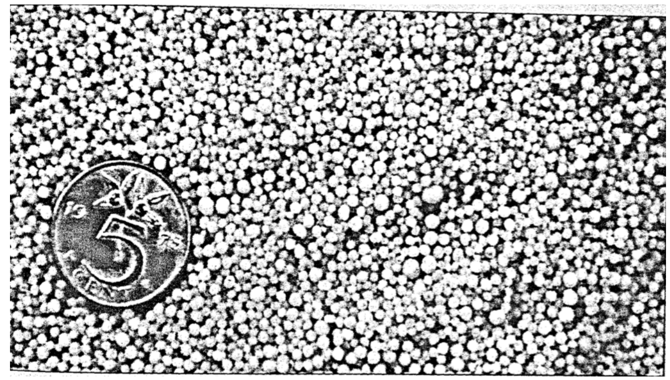
DHV Crystalactor®



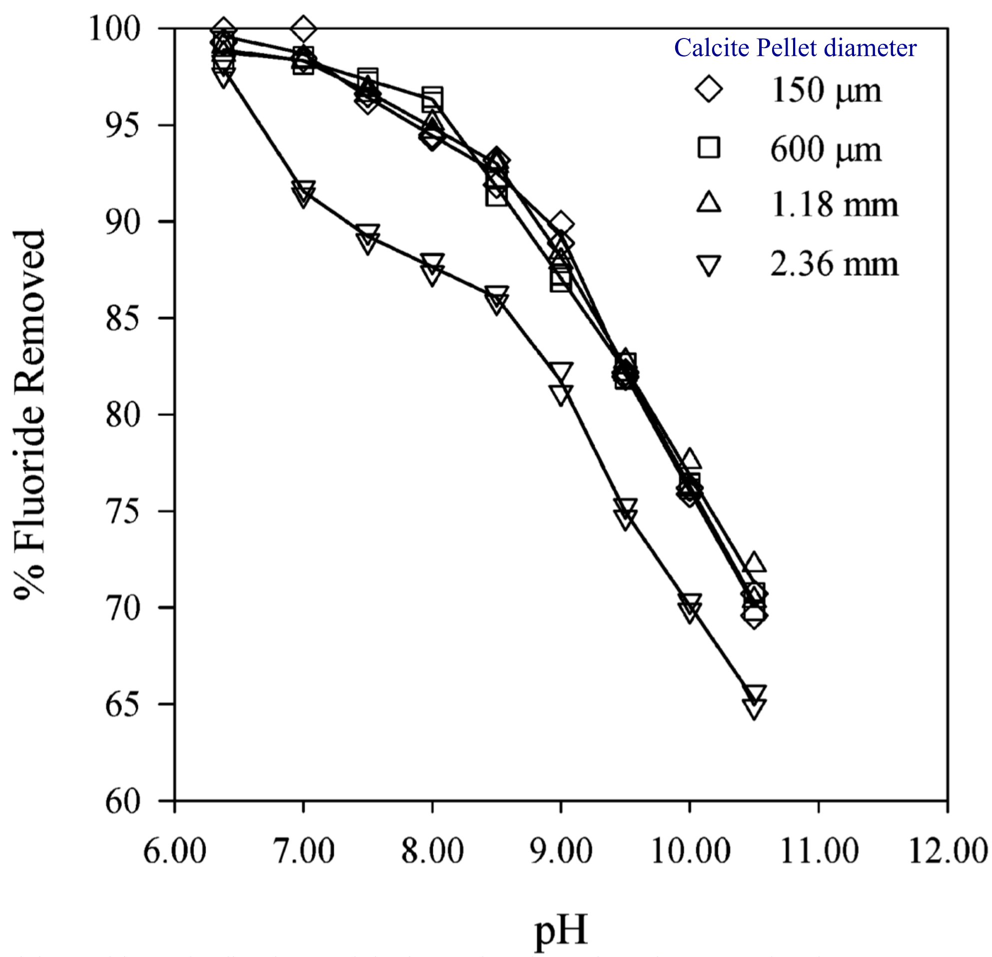
Dijk, J.C. and Wilms, D.A., Water treatment without waste material-fundamentals and state of the art of pellet softening, J Water SRT-Aqua,1991, 40, 263-280

Central Softening *in* Amsterdam





Fluoride Removal *in a* Calcite Column



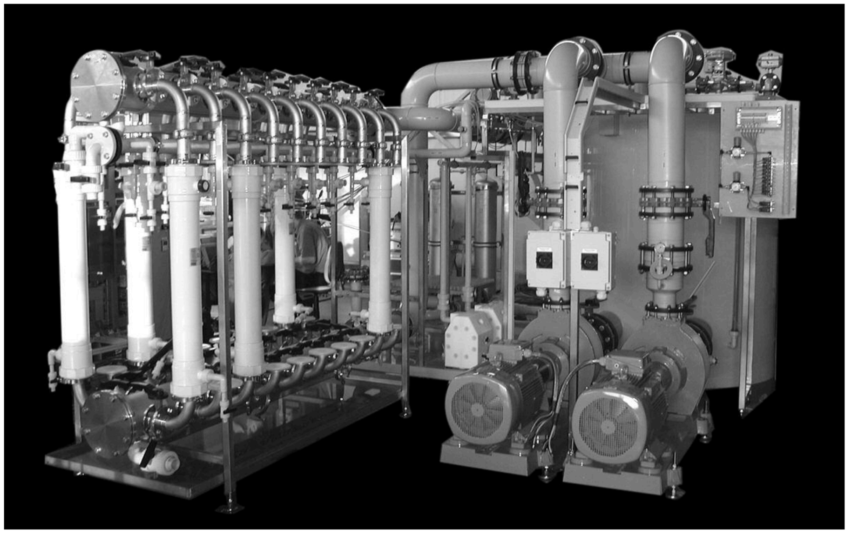
Turner, B., Fluoride removal by calcite: Evidence for fluorite precipitation and surface adsorption, J. Envi. Sci., 2005

CMP wastewater recycle process

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*

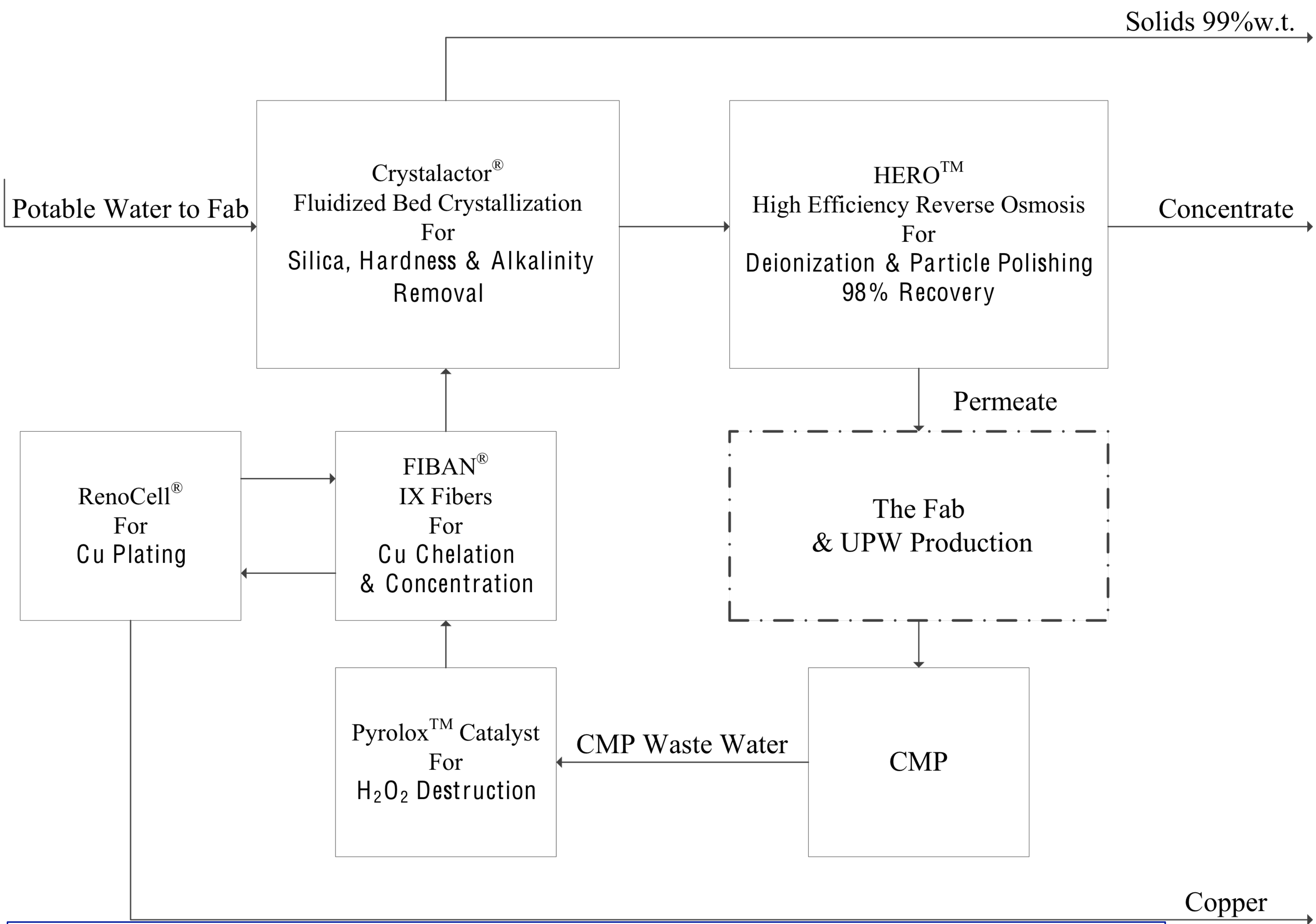
New CMP Wastewater Recycle Process

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

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

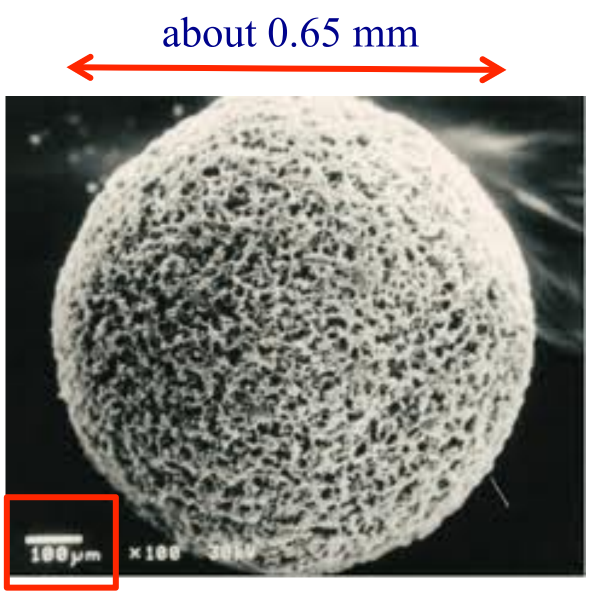
3) *Exploitation of new FIBAN® fibrous ion exchange technology to eliminate the need for expensive filtration or off-site regeneration of IX resin*

4) *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

FIBAN® Fibrous Ion Exchange Technology

Porous IX Bead



○*Most IX sites in IX bead interior*

○*Silica nanoparticles dissolve and foul bead during normal regeneration*

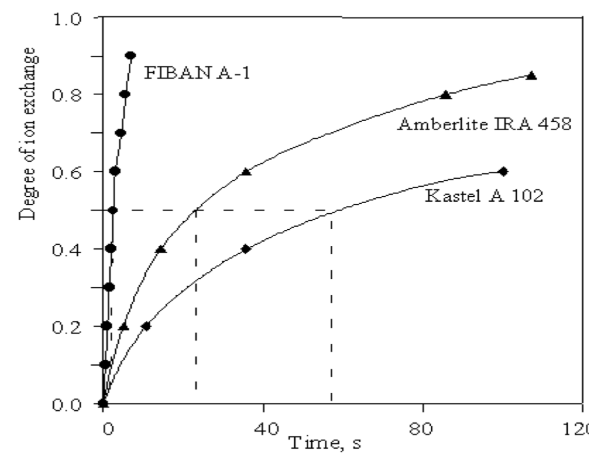
○*IX beads require off-site regeneration*

FIBAN® Filaments

✓*Most IX sites on FIBAN® surface*

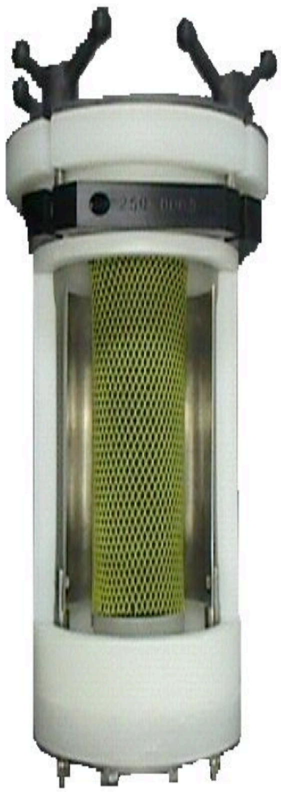
✓*FIBAN® can be regenerated at pH~1.5 (Copper Recovery)*

✓*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)



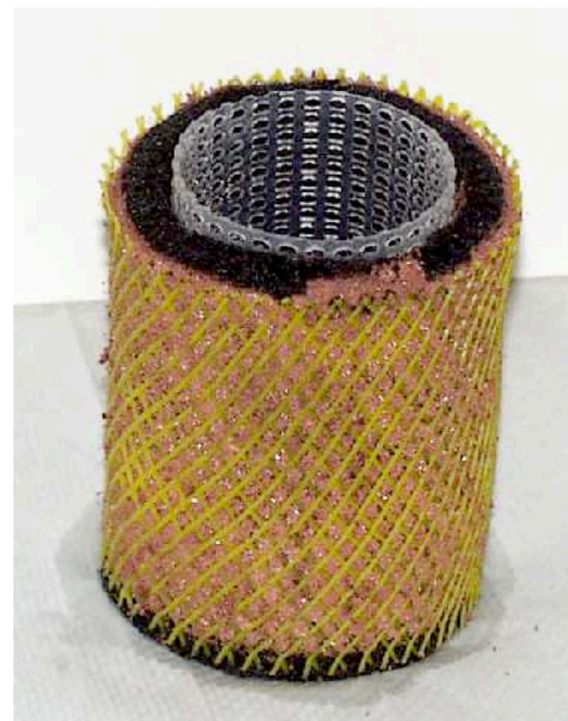
RenoCell®

Electroplating copper with zero acid consumption

Acid generation at anode
Cu deposition on cathode

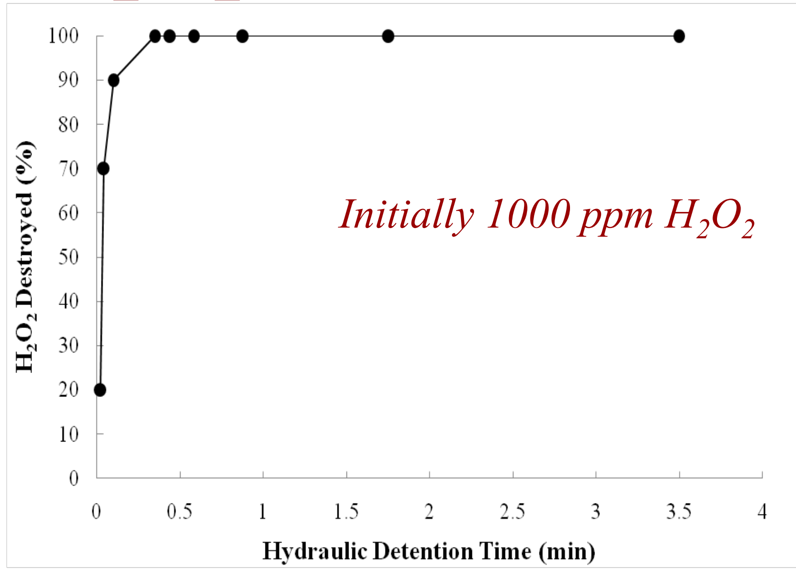
Throwaway carbon felt cathode (left)

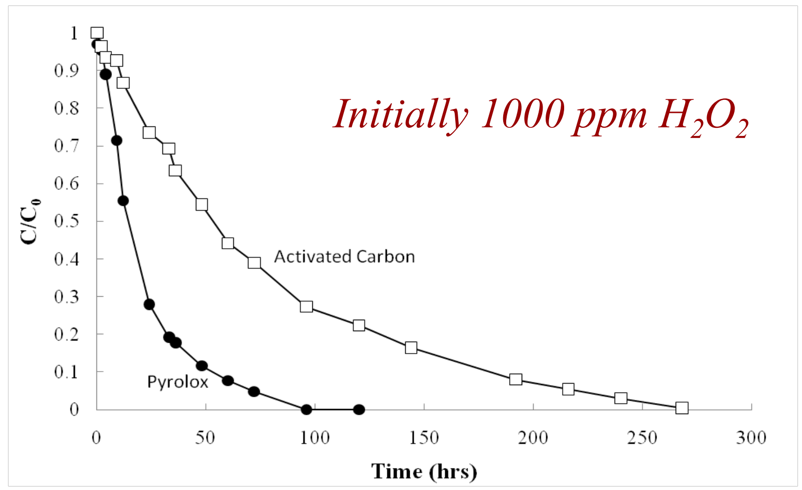
Copper laden carbon felt cathode from bench reactor (right)

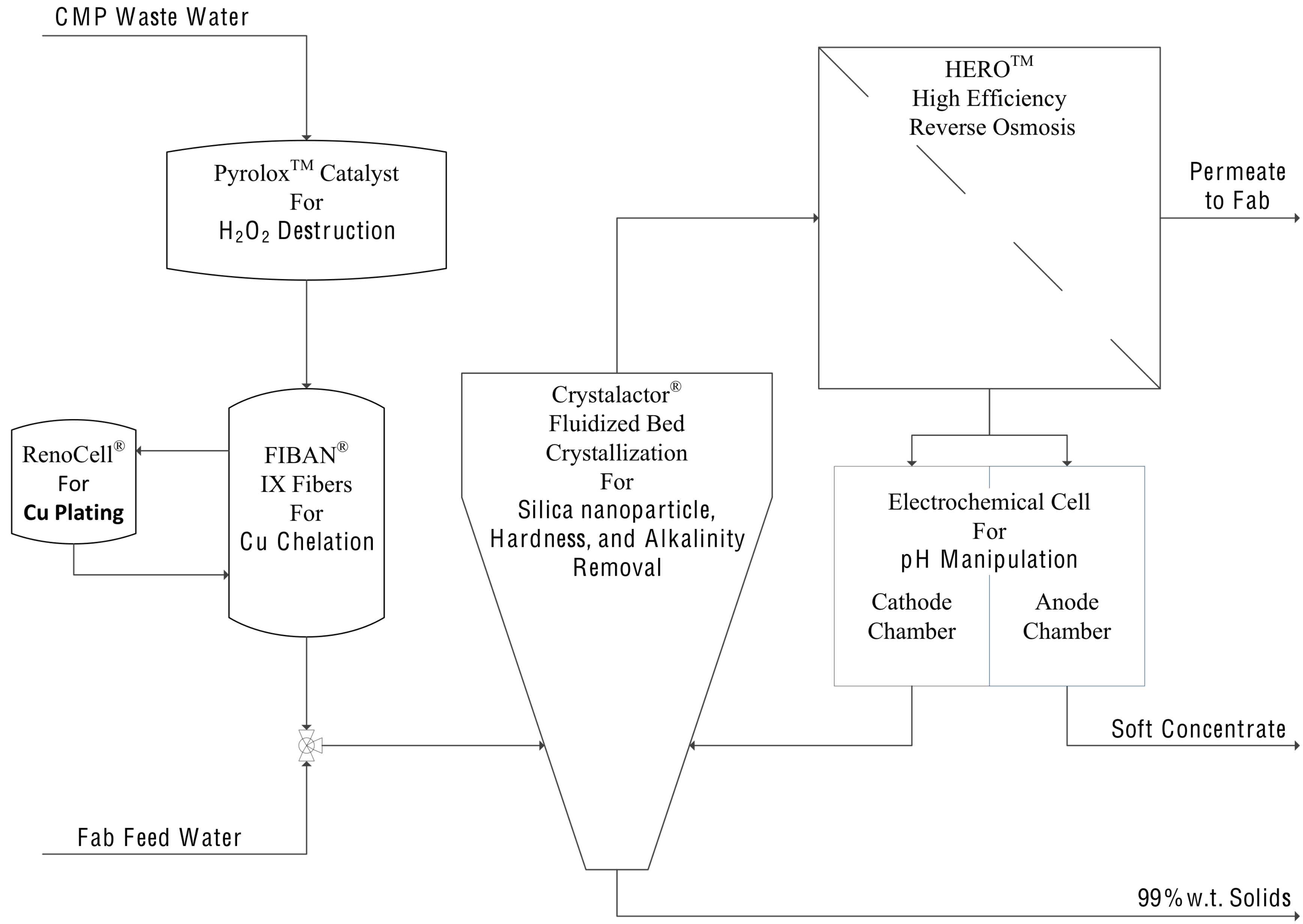


Catalytic Degradation of H_2O_2 with Pyrolox™

- *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*







SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
Teleseminar By: Jake Davis, PhD Candidate, University of Arizona

Conclusions

– The quality of water resources made available to the semiconductor industry will decrease with time.
– Regulation governing waste discharge will become more strict with time.
– Currently, the semiconductor industry can afford to not recycle wastewater. But, in the future, regulation will require the utilization of impaired water resources.

Acknowledgements

- Intel Corporation
- SRC/SEMATECH Engineering Research Center
- Don Hooper and Dan Hodges at Intel
- Advisers:
    - Dr. Jim Farrell
    - Dr. Jim Baygents