Evaluation of Alternatives to Domestic Ion Exchange Water Softeners

July 11, 2013

WateReuse Research Foundation Webcast Series

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The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water.

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A Few Notes Before We Get Started...

- Today's webcast will be 75 minutes.
- You will be able to download a PDF of today's presentation when you complete the survey at the conclusion of this webcast.
- There are 1.25 Professional Development Hours available for this webcast.
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WATEREUSE RESEARCH

Today's Presenters

Timothy M. Thomure, PE, PMP

- Water Reuse Practice Lead for HDR Engineering, Inc.
- 20 years of experience working in public utilities, private industry, and consulting
- Current President of WateReuse Arizona and Chair of the Water Reuse Committee of the AZ Water Association

Peter Fox, PhD

- Professor of Environmental Engineering at Arizona State University
- Best known for his work on groundwater recharge, indirect potable reuse, and salinity as it relates to such systems
- Served on the Executive Committee that wrote the National Roadmap for Desalination and Water Purification

Evaluation of Alternatives to Domestic Ion Exchange Water Softeners

WateReuse Research Foundation Project 08-06

ASU Ira A. Fulton school of engineering

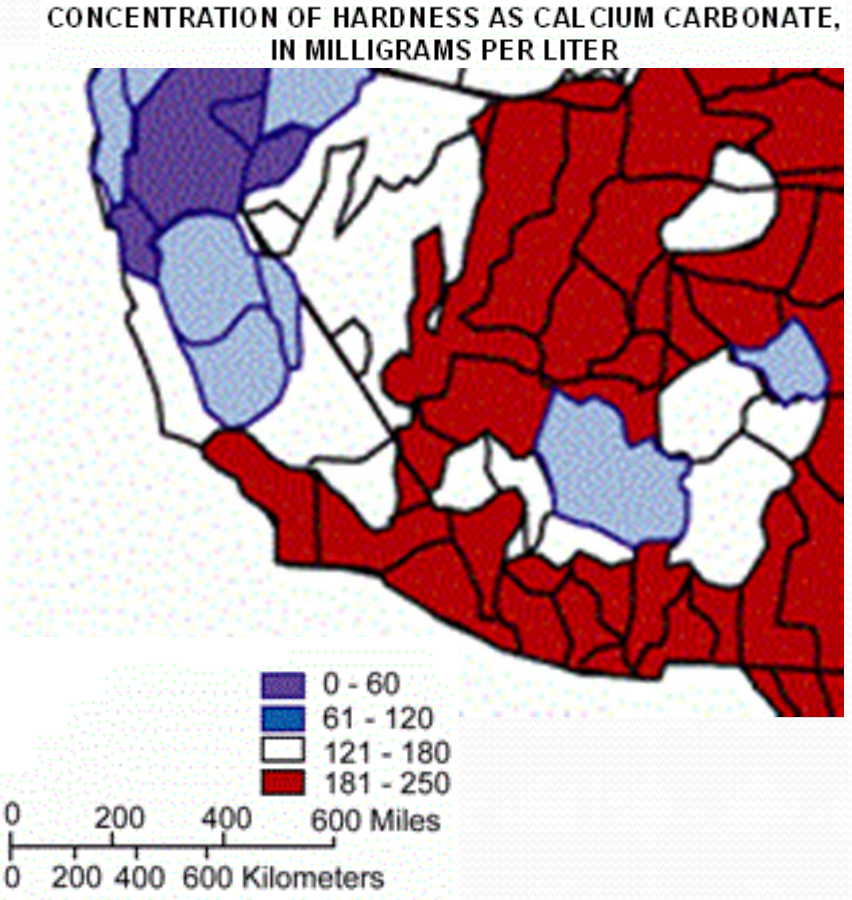
HDR

WATEREUSE RESEARCH

Water Quality and Reuse in the Southwest US

- Freshwater sources in the Southwest US are considered very hard ranging from 80 to 280 mg/L.

http://static.howstuffworks.com/gif/maps/pdf/NAM_US_THEM_Watersheds.pdf



http://water.usgs.gov/owq/hardness-alkalinity.html

Water Quality and Reuse in the Southwest US

- Hard Water Effects in the Home

Water Quality and Reuse in the Southwest US

- Consumers try to mitigate the effects of hard water by using water softening devices in their homes.
- The most common domestic water softening device uses ion exchange technology which releases additional salts to the waste stream.
- Consumers are reducing hardness in their homes but increasing TDS levels in reclaimed wastewater!

Water Quality and Reuse in the Southwest US

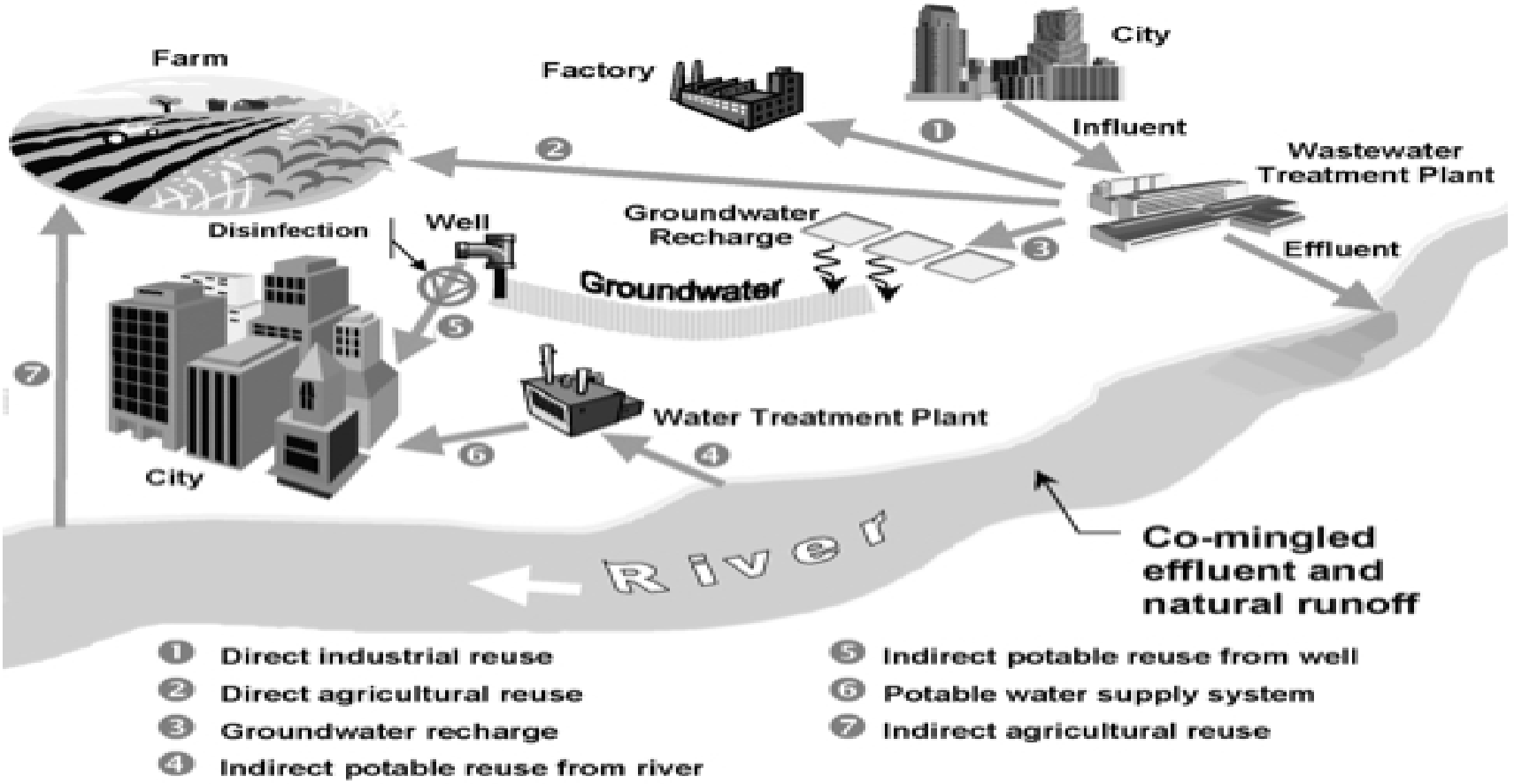
- TDS (salinity) is a measurement of total dissolved solids in water including inorganic (hardness, salts) and organic substances (pesticides, herbicides, etc.).

Sources of Salinity
• Natural minerals in rocks found in lakes, rivers, streams and aquifers
• Water from natural salt springs that enters into rivers, lakes and streams
• Agricultural fertilizers that drain from fields into rivers, lakes, streams and aquifers
• Water treatment chemicals such as chlorine that make water safe for human consumption
• **Home water treatment systems, like water softeners, that treat water for hardness**
• Cleaning chemicals
• Foods

Water Source	TDS in milligrams per liter
Salt River	580 mg/L
Verde river	270 mg/L
Central Arizona Project (CAP)	650 mg/L
Groundwater	200 - 5,000 mg/L
Reclaimed Water	Typically 300 - 500 mg/L higher than source water

Water Quality and Reuse in the Southwest US

- Water Reuse – A practice where recycled water is used for a direct beneficial purpose.



http://web.mit.edu/12.000/www/m2012/finalwebsite/solution/waterreuse.shtml

TDS effects on water reuse (examples)

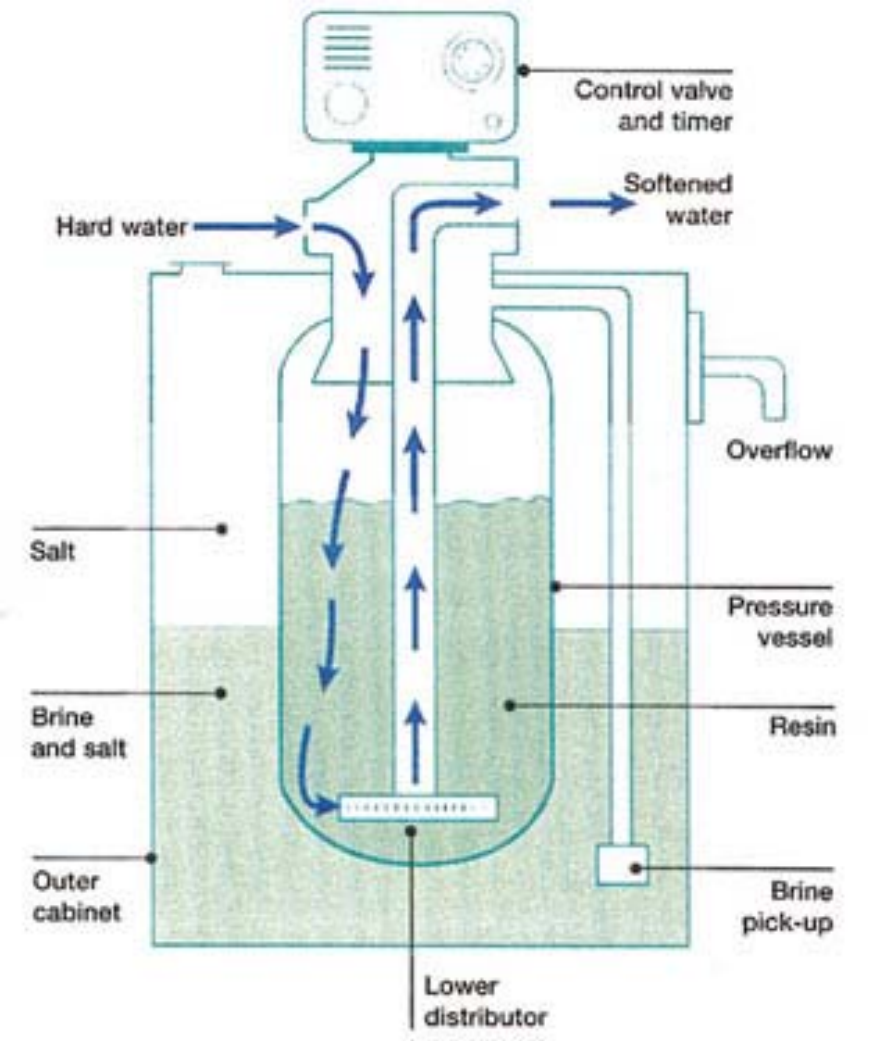
- Agriculture
  - Crop salt tolerance, reduction of crop yields
  - Additional water may be needed to flush salts from root zone
- Cooling Tower
  - Increased water usage
  - Possible equipment damage due to scaling

Study Objective

Provide technical data to identify credible **alternatives** to ion exchange water softeners that would provide consumers with the ability to reduce the impacts of hard water without creating the negative salinity impacts.

Ion Exchange Water Softening System

- The ion exchange unit removes hardness by exchanging sodium ions for the calcium and magnesium ions present in the water.
- It does this using resin beads that periodically need to be regenerated with a highly concentrated salt solution.
- There are two basic types of self-regenerating water softeners (SRWS): Timer Based and Demand Based.



http://www.sterlingsofteners.co.uk/index.asp?mid=49

Ion Exchange Water Softening System

- Discharge brine into wastewater systems
- These unnatural quantity of salts find their way into the environment and affect reuse applications.
- The use of no-salt water conditioning devices to reduce scale formation on domestic water heaters and other home appliances is one way society can improve the quality of remediated water.

Scale Prevention Technologies

- Chemical Treatment – Chemical Softening, Ion Exchange, Scale Inhibitors
- Physical Water Treatment (PWT) – Commonly used to describe the devices we will consider as alternatives to ion exchange. No chemicals added.
- PWT Devices tend to work by forming subicron crystals of calcium carbonate that remain suspended in water

Evaluation of Alternatives to Ion Exchange

- Many potential factors to consider
  - Scaling of Hot Water Heater
  - Scaling/streaking of sinks, toilets, dishes, etc.
  - Taste
  - Water Use
  - Energy Use – both treatment device and hot water heater

  This study will focus primarily on scaling since this can be scientifically quantified.

Quantifying Scale Formation

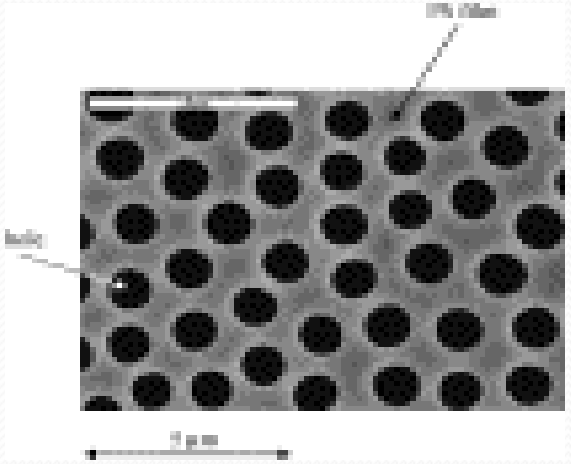
- DVGW – German Association of Gas and Water Boards is responsible for certifying technologies for safety, hygiene and performance capabilities.
- DVGW – W512 is the test used to determine effectiveness of water conditioning devices installed to prevent or reduce scaling in drinking water heating systems and secondary installations.
- The W512 testing protocol is the basis for our experimental methodology.
- Operate a system for twenty days and quantify scale formed in a water heater.

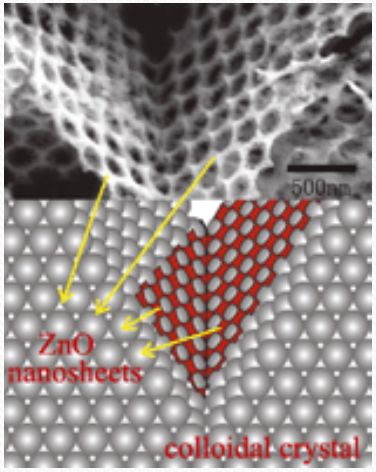
Physical Water Treatment Technologies

- Template Assisted Crystallization – Catalyzes the formation of sub micron crystals that remain suspended in the water
- Electrically Induced Precipitation – An applied current induces the formation of “soft” scale on an electrode that must be periodically cleaned
- Electromagnetic Devices – Appear to cause formation of soft precipitates that remain suspended in water (literature refers formation of aragonite or vaterite instead of calcite)

Template Assisted Crystallization

- Technology Has Many Different Applications – Relatively new to water treatment
- A Reaction is carried out on a template – usually a honeycomb polystyrene structure
- Can be used to make well ordered micrometric and nanometric structures
- ZnO nanosheets, Photonic Balls

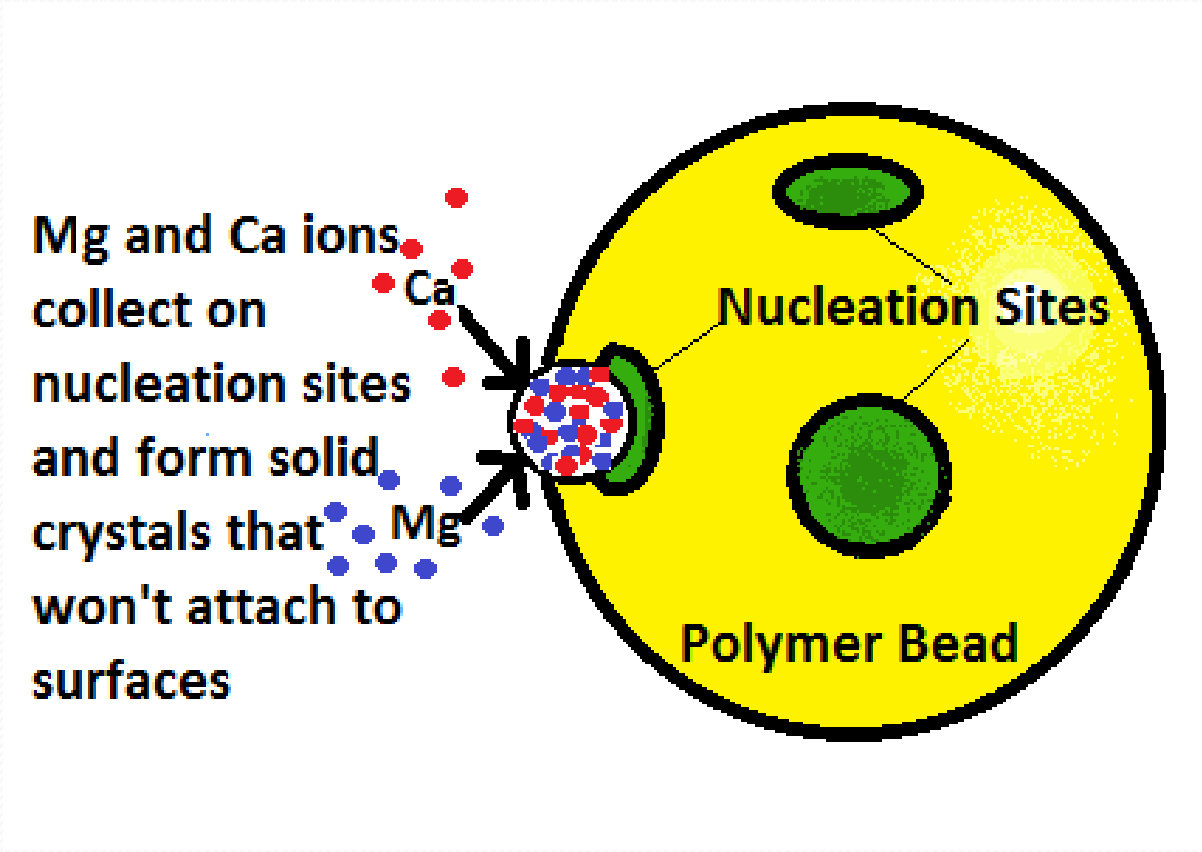




Template Assisted Crystallization

- Uses Polymeric Beads with nucleation sites to convert dissolved hardness into microscopic crystals
- Once crystals grow to the template size, the crystals are released and remain in the water without forming scale
- DVGW Certified
- Operates as a fluidized bed to maximize surface area and effectiveness
- Commercially available for a variety of flowrates.

Template Assisted Crystallization

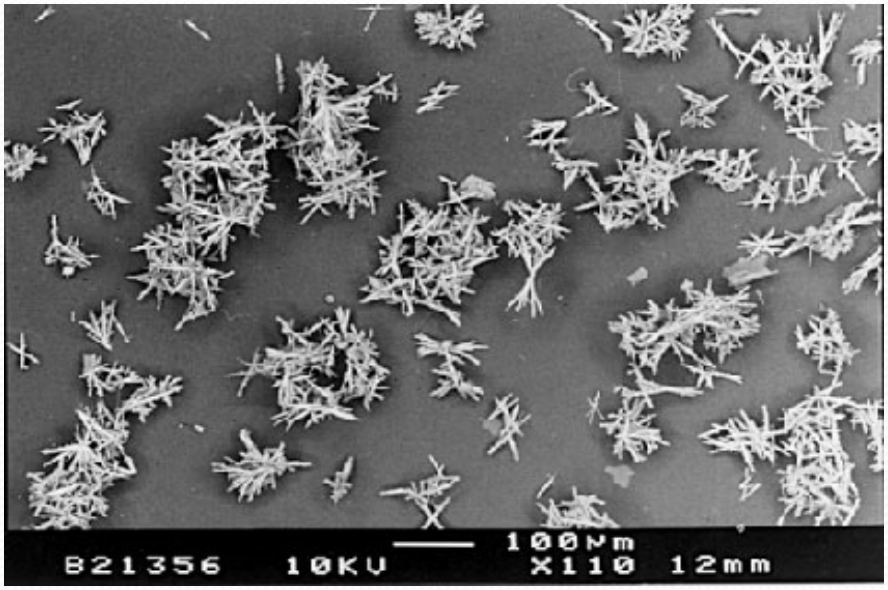


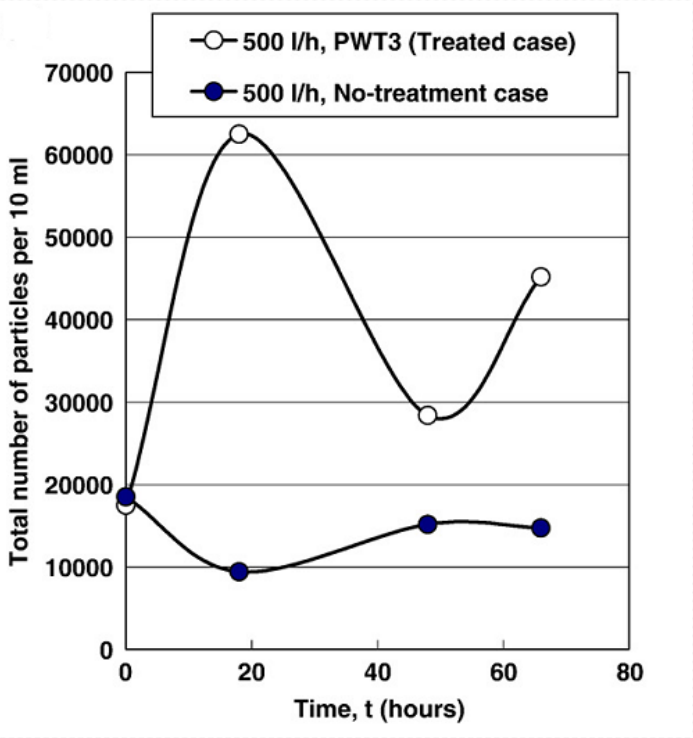
Electrically Induced Precipitation

- Uses Direct Current to form Soft Precipitate
- DVGW certified
- Maximum Power required – 100W
- Length of Operation may be limited since use of DC is dangerous
- Backwash Water is required to clean electrode – Process Control not clear – Manual Operation Required

Electrically Induced Precipitation

- $CaCO_3$ crystals appear to be aragonite – needle like crystals that do not form scale





Tijing et al, 2007

Electromagnetic Technologies

- Literature has mixed results – successful tests result in aragonite or vaterite instead of calcite
- Electromagnetic fields will cause separation of ions and Lorentz Force is a function of flow velocity

Hall Effect – Lorentz Force

Electromagnetic flowmeters (EMFs)

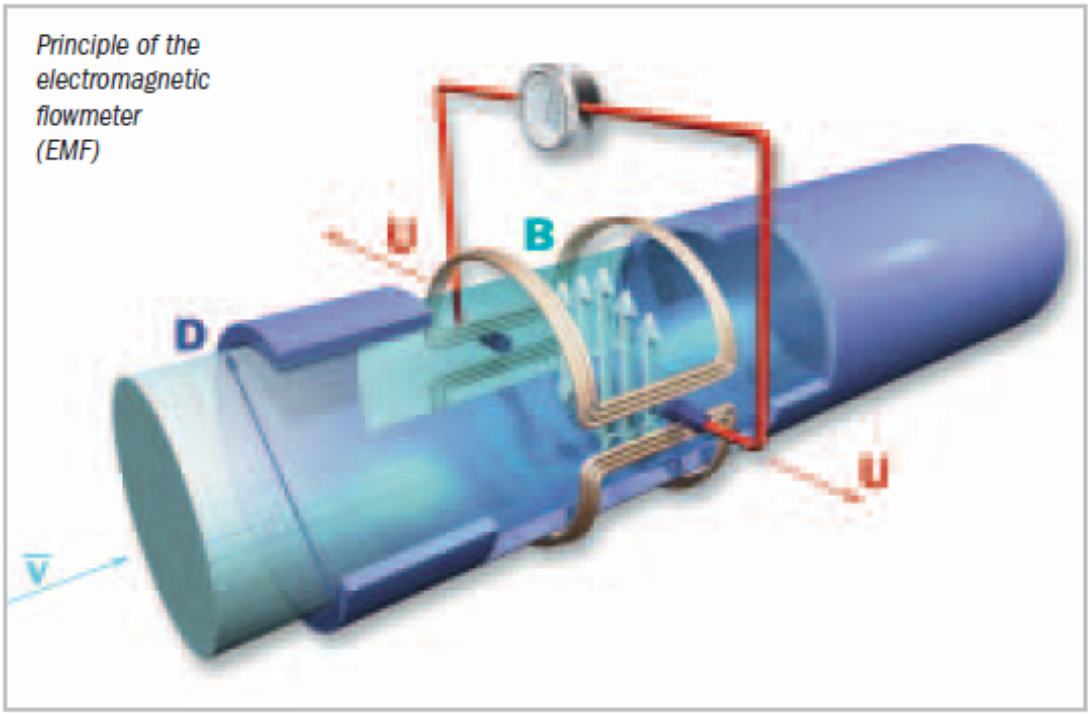
Friedrich Hofmann, Dipl.-Ing., D-47058 Duisburg

Principle and theory, in brief:

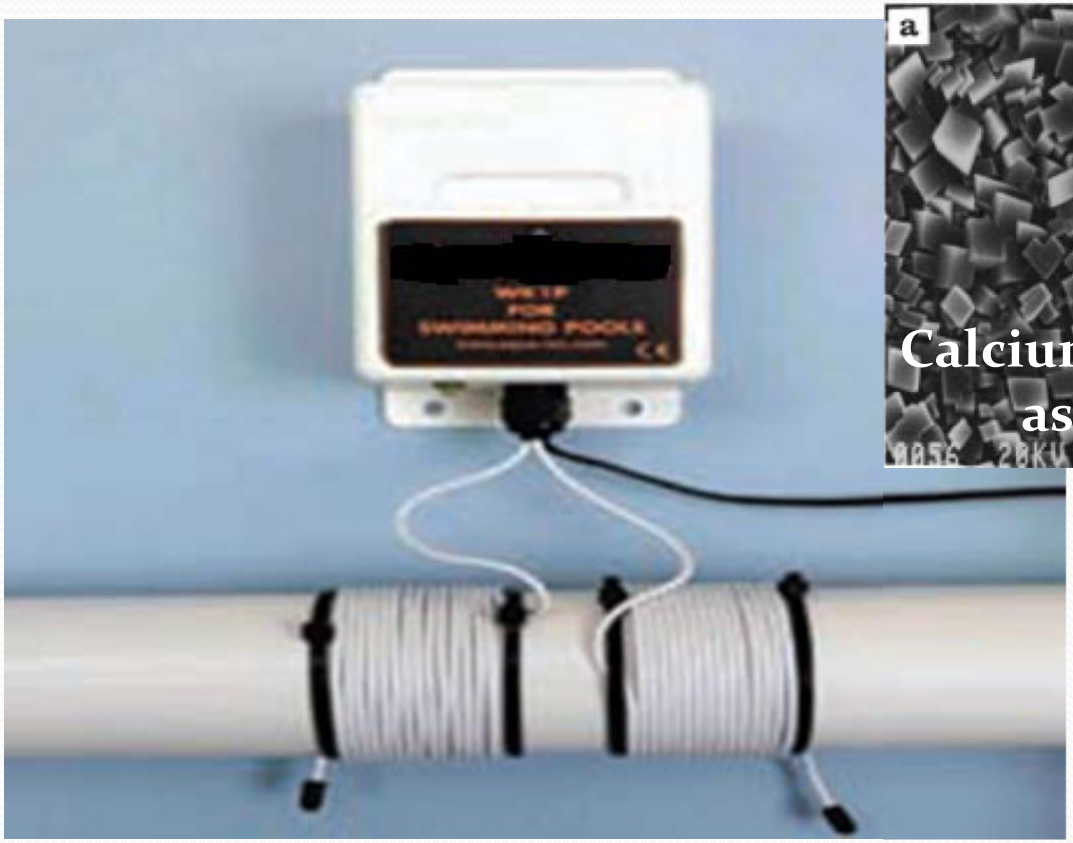
Principle

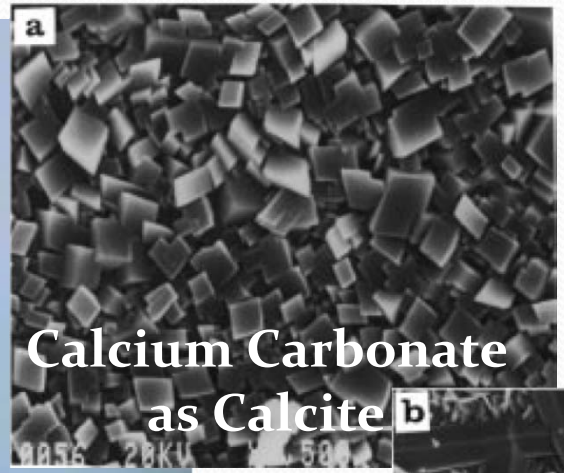
The figure shows the basic setup of an electromagnetic flowmeter (EMF) for completely filled pipelines.

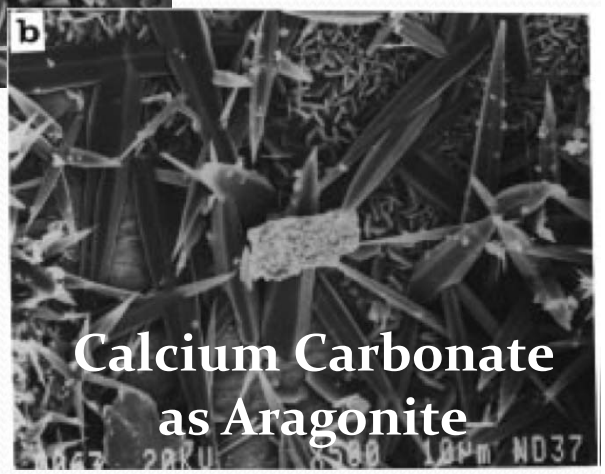
Principle of the electromagnetic flowmeter (EMF)



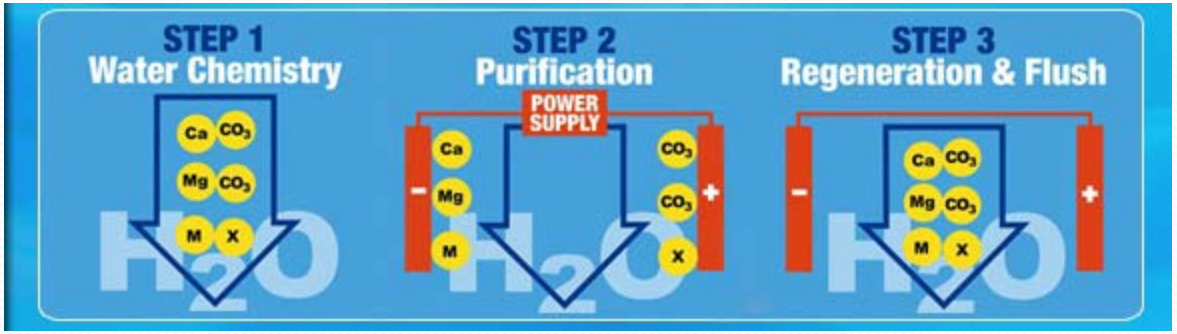
Electromagnetic Technologies







Capacitive Deionization



- Apply DC current – 2 amps at 110 V
- Ions move to anode and cathode and attach to carbon aerogel or new nanostructured material
- Once saturated, must regenerate and flush
- Citric Acid cleaning may be necessary
- Technology has been in development for 50 years

Capacitive Deionization

- Commercially Available for Whole House Treatment
- 80-95% Salt Removal
- 75% water recovery – is this acceptable?
- Semi-Automatic Citric Acid Clean
- Dial for Taste – level of removal can be controlled

Summary of Technologies Tested

- Template Assisted Crystallization – Scale Inducing

New to water industry and rapidly developing technology

No Power or Backwash required

Life of Media – recommended change 12-18 months

- Electrically Induced Precipitation – Scale Inducing

Relatively new to water industry

Power and periodic backwash required

Summary of Technologies Tested

- Capacitive Deionization – Technology in Development for 50 years with limited application

Requires Power and 25% reject water

Periodic Citric Acid Clean

Can control removal of salt for taste

- Electromagnetic Technologies – Been used for many years with sporadic documentation

Power required

No backwash required

Filters sometimes sold with the technology

Direct Comparison of Technologies

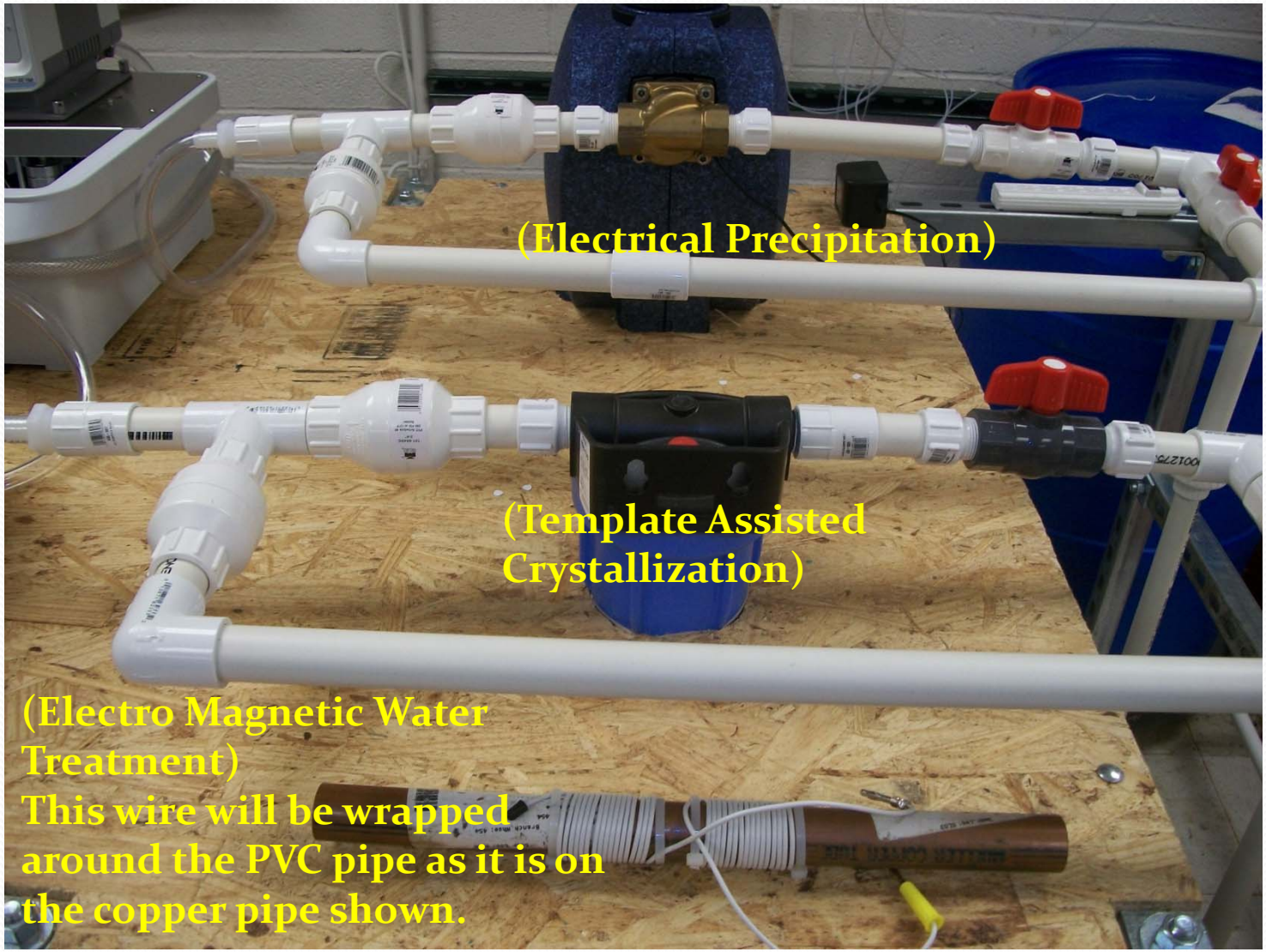
Technology	Max Power Required	Backwash Required	Cost	Salt Addition Required
Capacitive Deionization	220W	Yes	High	No
Electrically Induced Precipitation	100W	Yes	High	No
Template Assisted Crystallization	None	No	Moderate	No
Magnetic Water Treatment	8W	No	Low	No
Ion Exchange	13.5W	Yes	Moderate	Yes

Testing Methodology

- Protocol based on DVGW W512 test to assess control of scale formation
- Pump 130 L/d of water through an electronically heated 10-L reservoir for 20 days
- After test is complete, determine the quantity of scale formed on the heating element and the reservoir
- The test has a specific calculation to determine if a scale prevention device will be certified – this is based on a specified water quality and is not applicable to our testing where different waters will be tested

Testing Apparatus: Side View

Alternative Conditioning Devices



DVGW W512 Protocol

- Requires a temperature of 80°C. Domestic water heaters operate between 40-60°C. It would be more realistic to operate the tests at 60°C.
- Requires a low watt density < 5 W/cm². This eliminates effects that can occur at higher watt densities and ensures an even distribution of heat and scale formed.

Assessment of Scale Formation

- The quantity of calcium and magnesium in any scale formed is quantified by dissolution in acid and subsequent analysis
- Scale on the Heating Coil and the Container Walls is quantified in terms of the number of moles of Ca and Mg ions
- An effectiveness factor is calculate by comparing the results with a treatment device with results using untreated water

Effectiveness Factor (EF)

$$EF = \frac{(Ca + Mg)M \text{ untreated} - (Ca+Mg)M \text{ treated}}{(Ca + Mg)M \text{ untreated}}$$

The DVGW certifies a device with an EF greater than 0.8

For this study the EF will be used as a relative measure without applying any pass fail criteria.

Waters Tested

- City of Tempe Tap water – Salt River (180 mg/l of hardness as $CaCO_3$) at 60°C and 80°C
- Colorado River Water – Central Arizona Project treated at Scottsdale Water Campus (150-220 mg/L of hardness as $CaCO_3$)
- Groundwater – South Scottsdale at Pima Park Treatment Facility – Treated by Air Stripping (450-500 mg/L of hardness as $CaCO_3$)

RESULTS: Tempe Tap – Untreated

RESULTS: Tempe Tap – Template Assisted Crystallization

RESULTS: Tempe Tap – Electromagnetic

RESULTS: Tempe Tap – Electrically Induced Precipitation

TABLE 6: TOTAL CALCIUM SCALE COLLECTED

Overall Results

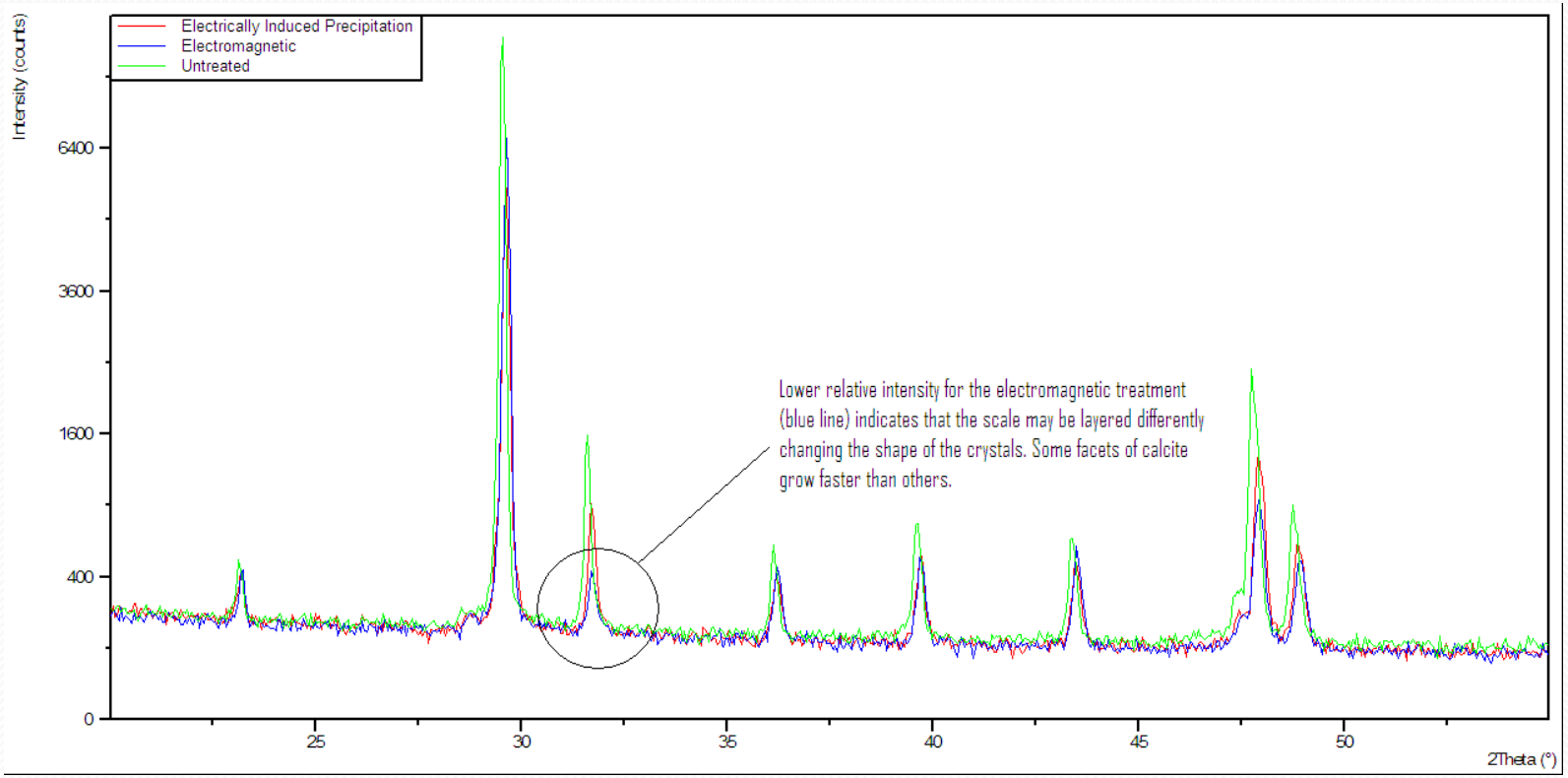
SCALE TOTALS (g CaCO3)

Treatment Type	Tempe 80 °C	Tempe 60 °C	CAP 80° C	Scottsdale GW 80° C
No Treatment	13.36	9.97	20	29.75
TAC	0.48	0.33	0.65	3.2
EIP	6.72	5.56	9.84	15.4
MAG	7.56	5.28	10.23	16.7

Testing Summary

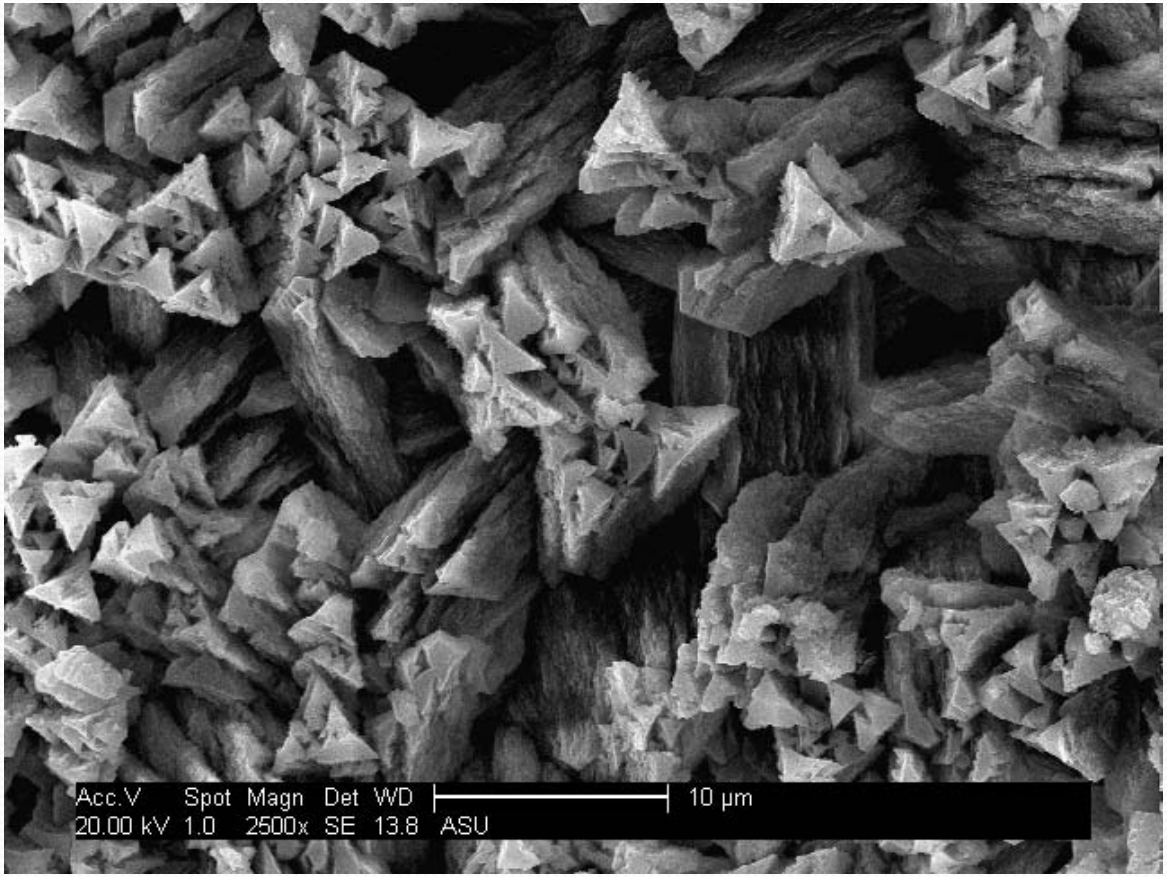
- Template Assisted Crystallization worked best
- Both Electromagnetic treatment and electrically induced precipitation reduced scale formation significantly. The scale formed was “soft” scale that easily brushed off. The test does not determine long term accumulation

X-Ray Diffraction



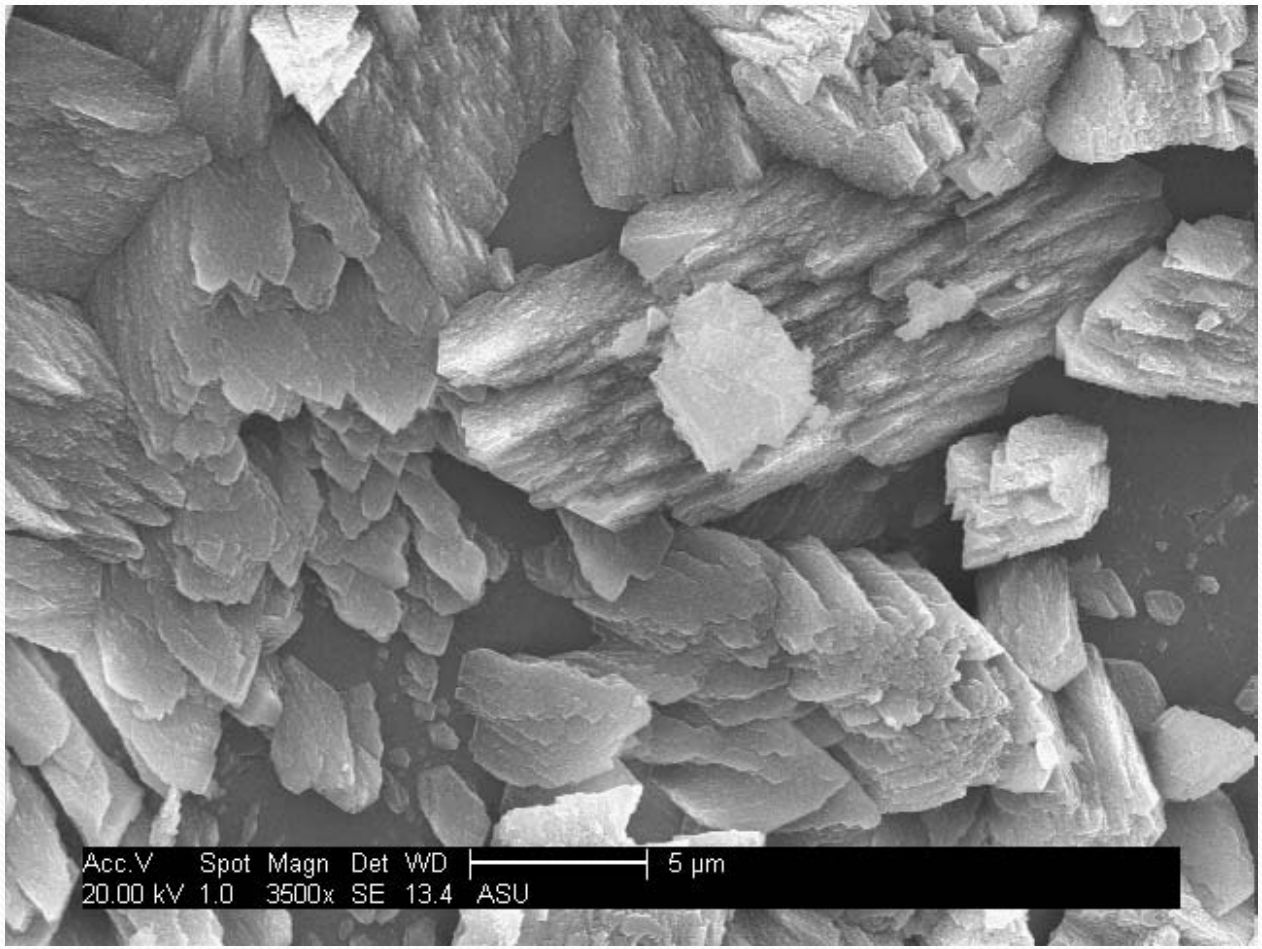
All have calcite patterned peaks but relative intensities are different

Control: Crystals Aligned

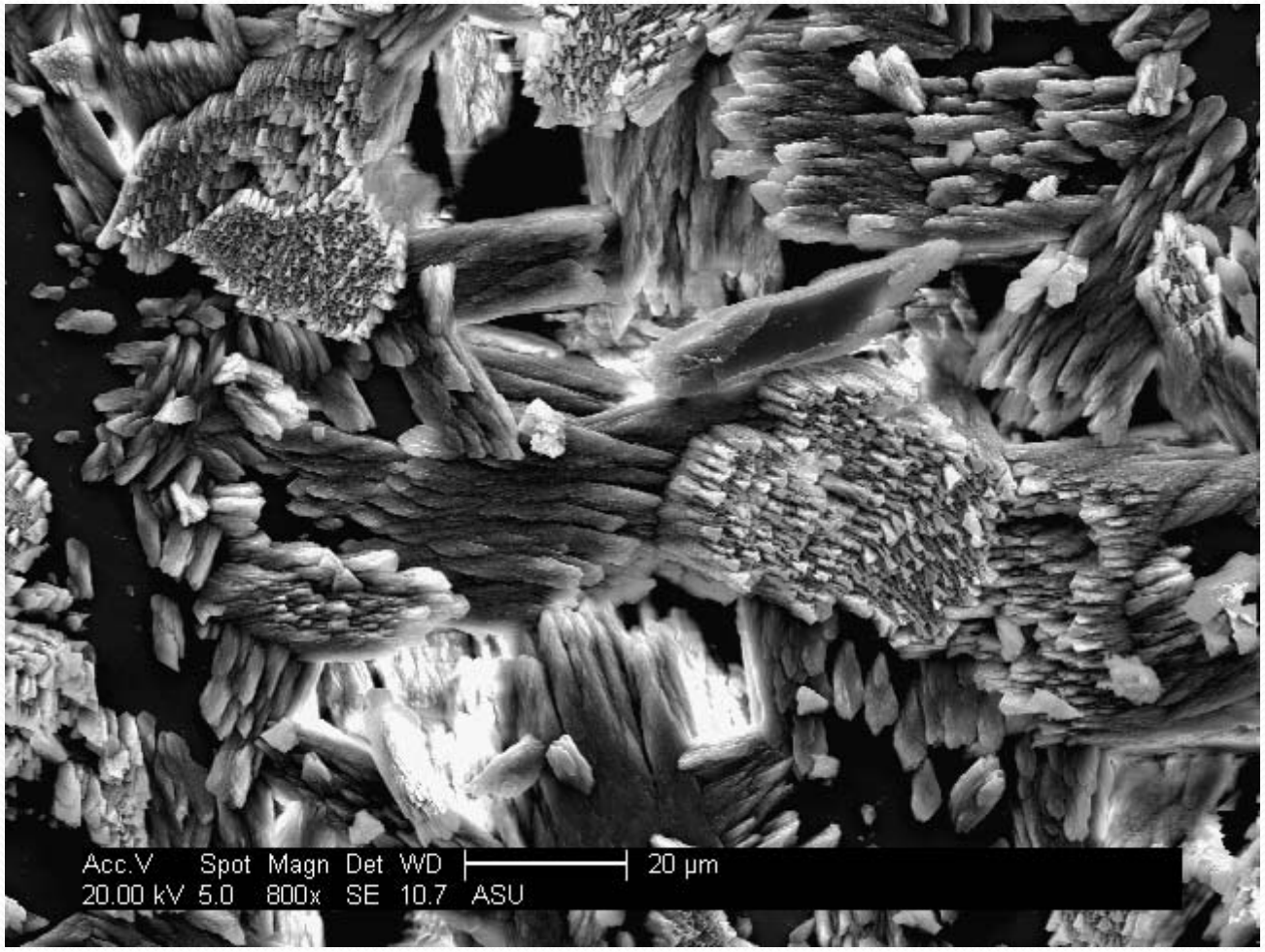


Element	*Wt%*	*At%*
CK	11.68	22.27
OK	35.13	50.29
MgK	01.08	01.02
AuM	07.38	00.86
CaK	44.74	25.57
Matrix	Correction	ZAF

EIP: Crystal Orientation Random



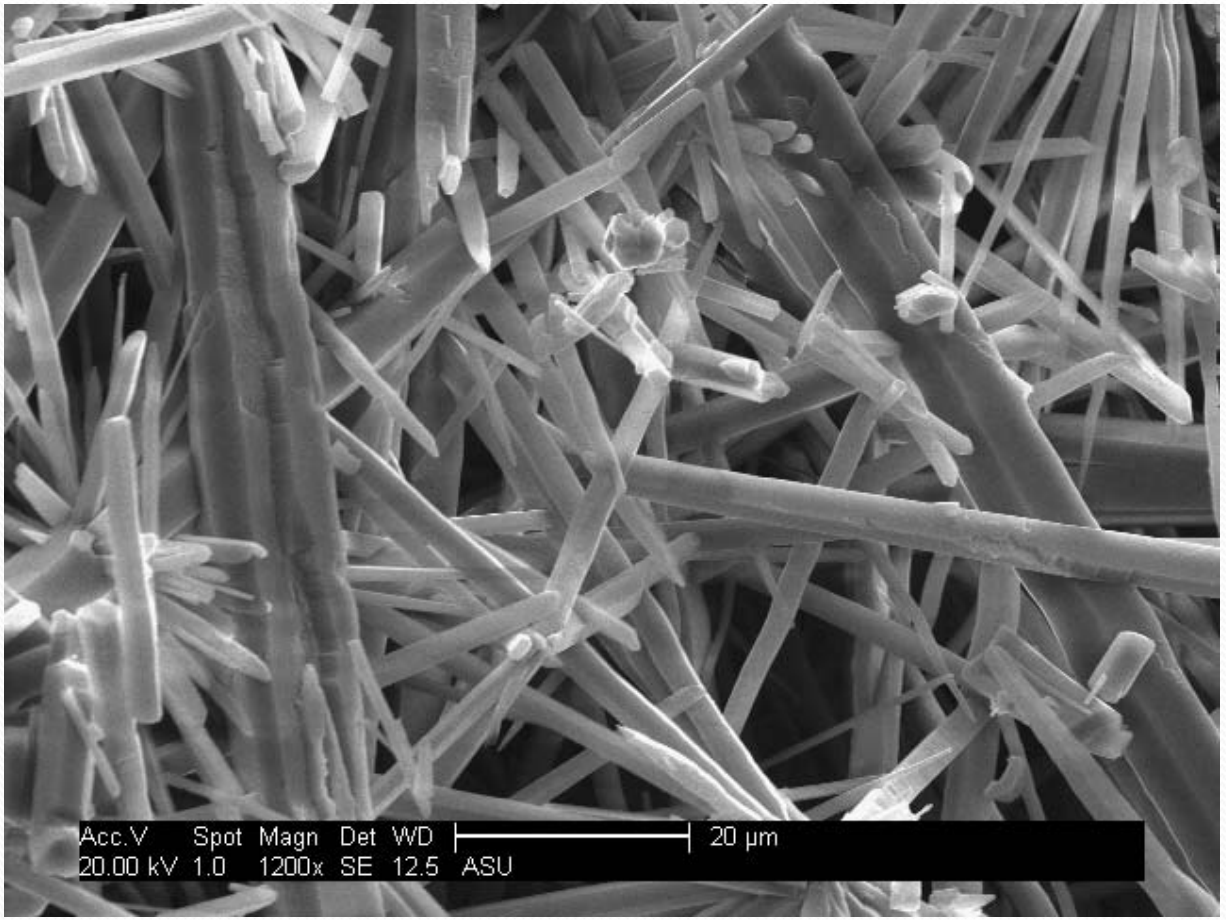
MAG: Crystal Orientation Random



Scottsdale Groundwater Element

Untreated

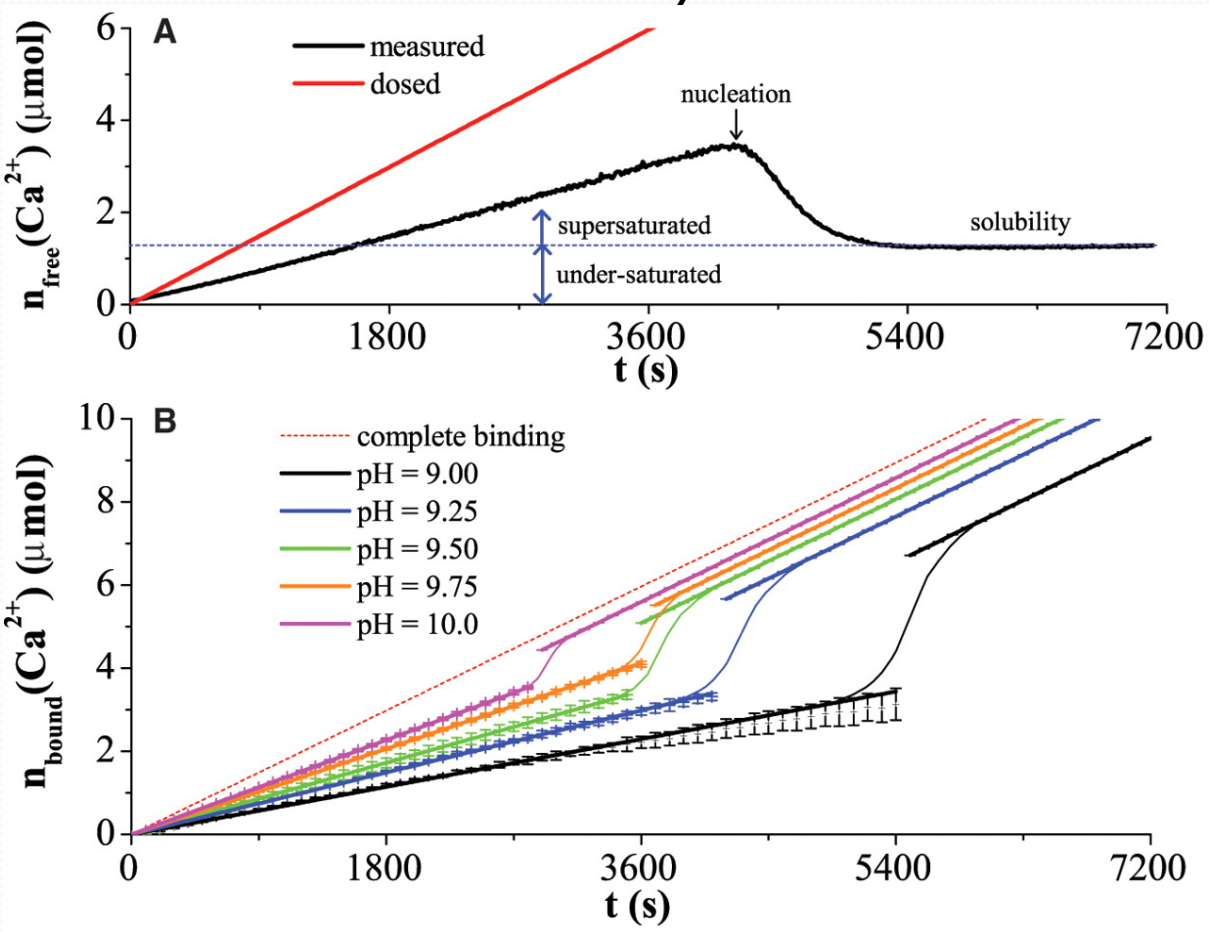
Scottsdale Control – Aragonite – High Scaling Potential



Summary of Crystallization

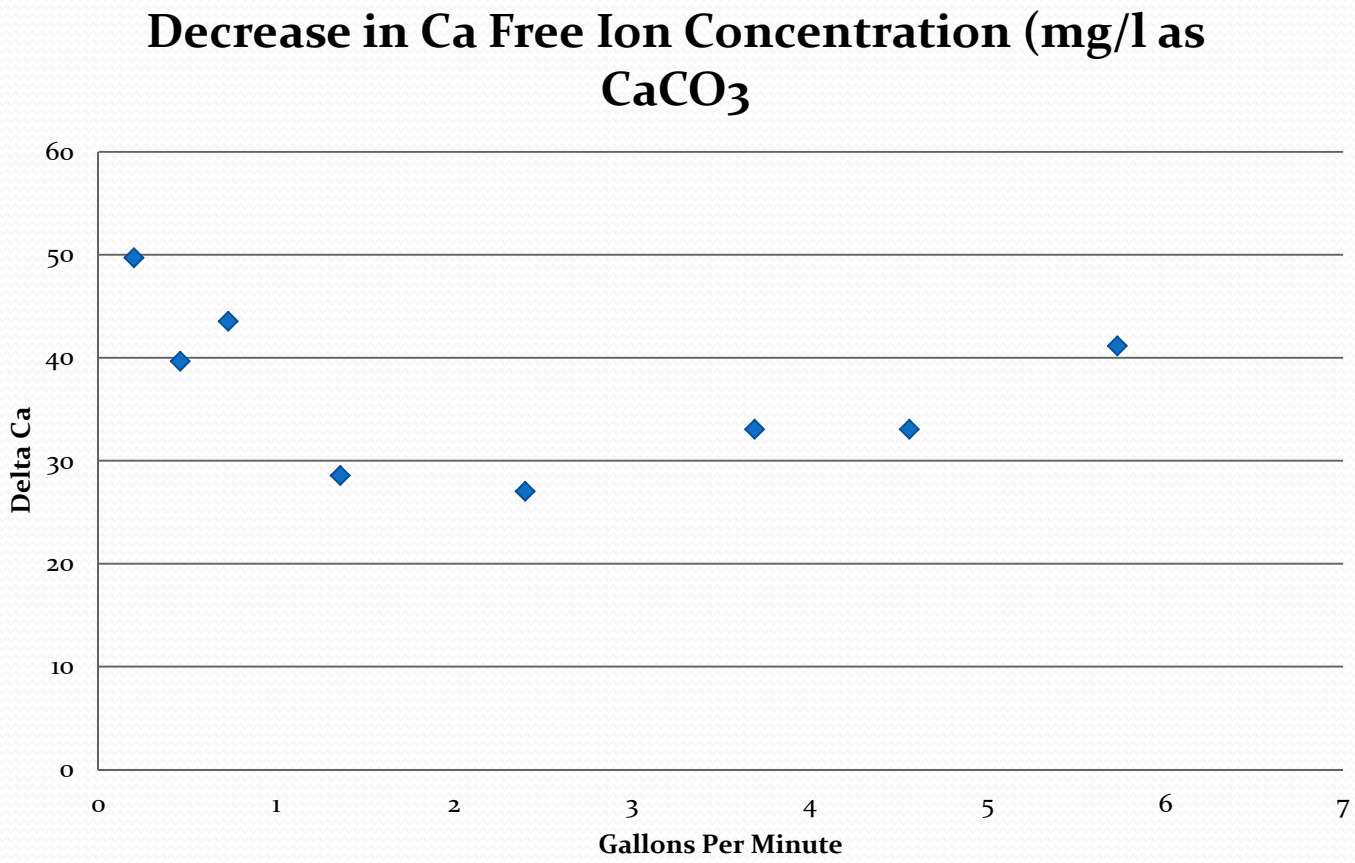
- “Hard” Scale forms when nucleation is initiated uniformly on the heating element – aligned crystals are stacked upon one another.
- Soft Scale – deposition of suspended crystals causes random orientation of crystals in scale
- Arogonite formed instead of calcite with the highest scaling potential water

Fig. 1. (A) Development of the free calcium ions measured by the calcium ion selective electrode (black line) at pH = 9.25 in comparison with the dosed amount of calcium ions (red line).



D Gebauer et al. Science 2008;322:1819-1822

Template Assisted Crystallization – Change in Free Ca ions as a function of flowrate



Free Ca = 90 mg/l as $CaCO_3$ Initially

Device rated at 1-2 gpm

What Does A Decrease in Free Calcium Ion Concentration Imply?

- There is no change in the total Calcium Concentration as measured by EDTA method
- Therefore the calcium is present in solution
- Hard waters have a positive Langelier Saturation Index - supersaturated with respect to calcium carbonate

LSI Calculations – Function of Free Calcium Ions and Bicarbonate (Alkalinity)

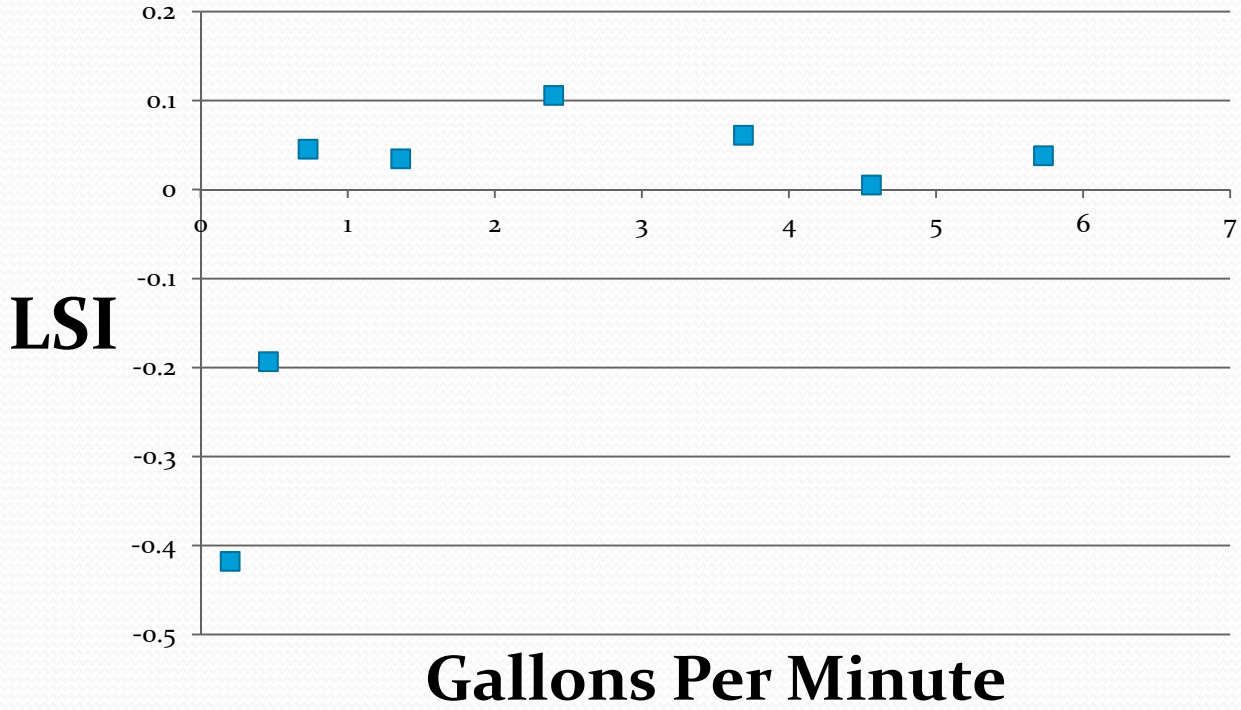
- $LSI = pH - pH_s$
- Where $pH_s = pK_{a2} + pK_{so} + p\{Ca^{2+}\} + p\{HCO^{3-}\}$
- Indications:
- LSI < 0: Water is undersaturated with respect to calcium carbonate. Undersaturated water has a tendency to remove existing calcium carbonate protective coatings in pipelines and equipment.
- LSI = 0: Water is considered to be neutral. Neither scale-forming nor scale removing.
- LSI > 0: Water is supersaturated with respect to calcium carbonate ($CaCO_3$) and scale forming may occur.

Calcium Ion Selective Electrode and PWT

- Decrease in Free Calcium Ion Concentration has been observed for electromagnetic treatment devices
- Langelier Index Calculations reveal that a supersaturated water can become undersaturated (scale reducing) when subject to PWT
- Sub-micron crystals are metastable and free calcium ion concentration returns to initial value in 2-3 days

Template Assisted Crystallization – LSI adjusted for reduction in free Calcium Ion Concentrations

Initial LSI = 0.41



Conclusions

- All alternative devices tested were effective at reducing scale.
- The most promising technology is the template assisted crystallization with scale reductions of over 90%.
- Soft-scale can result when deposition of crystals on a surface occurs
- Calcium ion selective electrodes may be used to assess and/or monitor the efficacy of physical water treatment devices

Acknowledgments

- WateReuse Research Foundation
- California State Water Resources Control Board, California Energy Commission, and California Department of Water Resources
- Cities of Hollister, Phoenix, Scottsdale, Tempe, and Tucson
- Santa Clara Valley Water District
- County Sanitation Districts of Los Angeles
- Southern California Salinity Coalition
- Many Industry Partners

Questions?

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