# Evaluation of Alternatives to Domestic Ion Exchange Water Softeners WRF-08-06

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# 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.

# Related Factors not Considered in this Study

- Domestic Water Heating uses more energy than urban water/wastewater treatment and distribution.
- In 2008, CDC acknowledged more waterborne disease from premise plumbing than from traditional pathogens (Legionella, mycobacterium).
- Recent research shows autotrophic growing on sacrificial anodes add AOC in hot water heaters.
- Scale certainly affects these factors.

# 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 what we are basing our experimental methodology on.
- Operate a system for twenty days and quantify scale formed in a water heater – more later.

# 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 may be classified as scale inducing or scale preventing.

# Scale Inducing Technologies

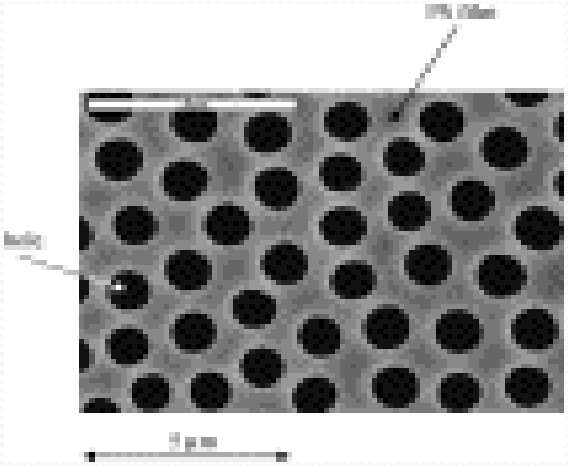
- These technologies work by inducing scale to form before a hot water heater thereby reducing the scale forming potential of the water.
- Template Assisted Crystallization – Catalyzes the formation of sub micron crystals that remain in the water as colloidal matter
- Electrically Induced Precipitation – An applied current induces the formation of “soft” scale on an electrode that must be periodically cleaned

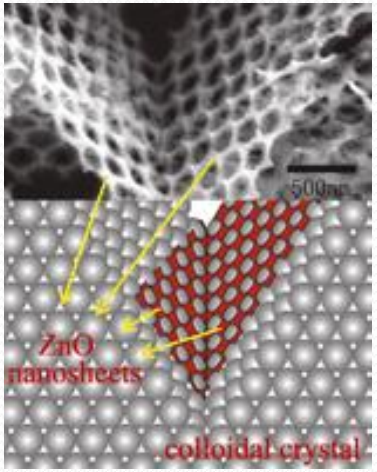
# Scale Preventing Technologies

- These technologies modify the water content to prevent scale formation.
- Capacitive Deionization – Reduces Concentrations of all ions to reduce scale formation
- Electromagnetic Devices (???) – Claim to cause formation of soft precipitates that remain colloidal (amorphous aragonite and vaterite instead of crystalline calcite)
- Other Static Devices – claim to cause effects similar to electromagnetic devices

# Template Assisted Crystallization

- Technology Has Many Different Applications – Relatively new to water treatment
- A Catalytic 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

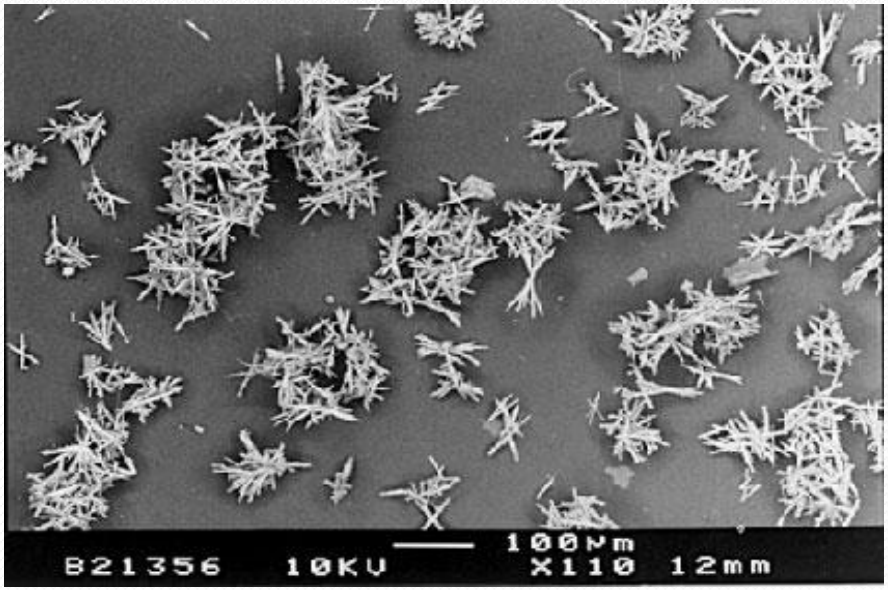
- Uses Polymeric Beads with nucleation sites to convert dissolved hardness into microscopic crystals
- Once crystals grow to the template size, the crystals are released and remain in the water without forming scale
- Calcite or Aragonite???
- DVGW Certified
- Operates as a fluidized bed to maximize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

# Electrically Induced Precipitation

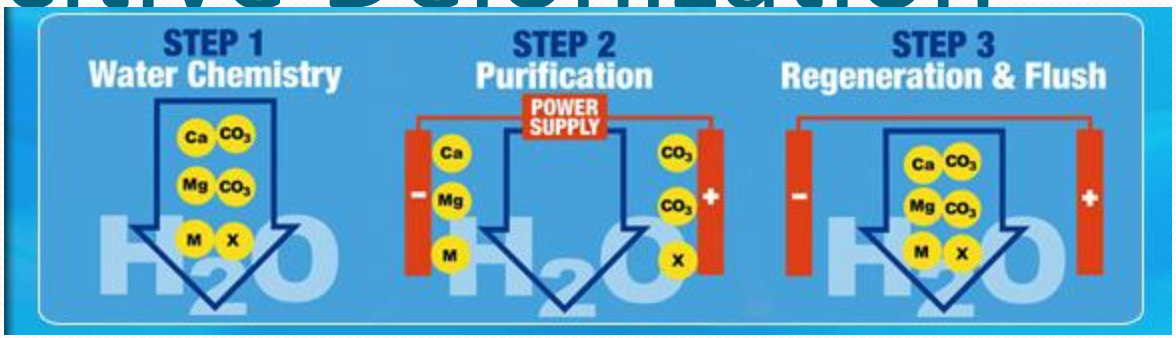
- Uses Direct Current to form Soft Precipitate
- DVGW certified
- Maximum Power required – 100W
- Length of Operation may be limited since use of DC is dangerous
- Backwash Water is required to clean electrode – Process Control not clear

# Electrically Induced Precipitation - Claims

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



# Capacitive Deionization –




- Apply DC current – 2 amps at 110 V
- Ions move to anode and cathode and attach to nanomaterials?
- 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 – where do we set it?

# Electromagnetic Technologies

- Literature has mixed results – successful tests result in aragonite or vaterite instead of calcite
- In theory, a magnetic field should not affect water but "structured" distilled water has been documented
- Recent studies have shown that dissolved oxygen may play a role – dioxygen is paramagnetic
- Silica may also play a role in scale prevention according to some studies
- Carbonate might also be important

# Electromagnetic Technologies

- Basic Device is a wire wrapped around a pipe that transmits electronic frequencies (magnetic field) to cause a physical change

# Summary of Technologies

- 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

- 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

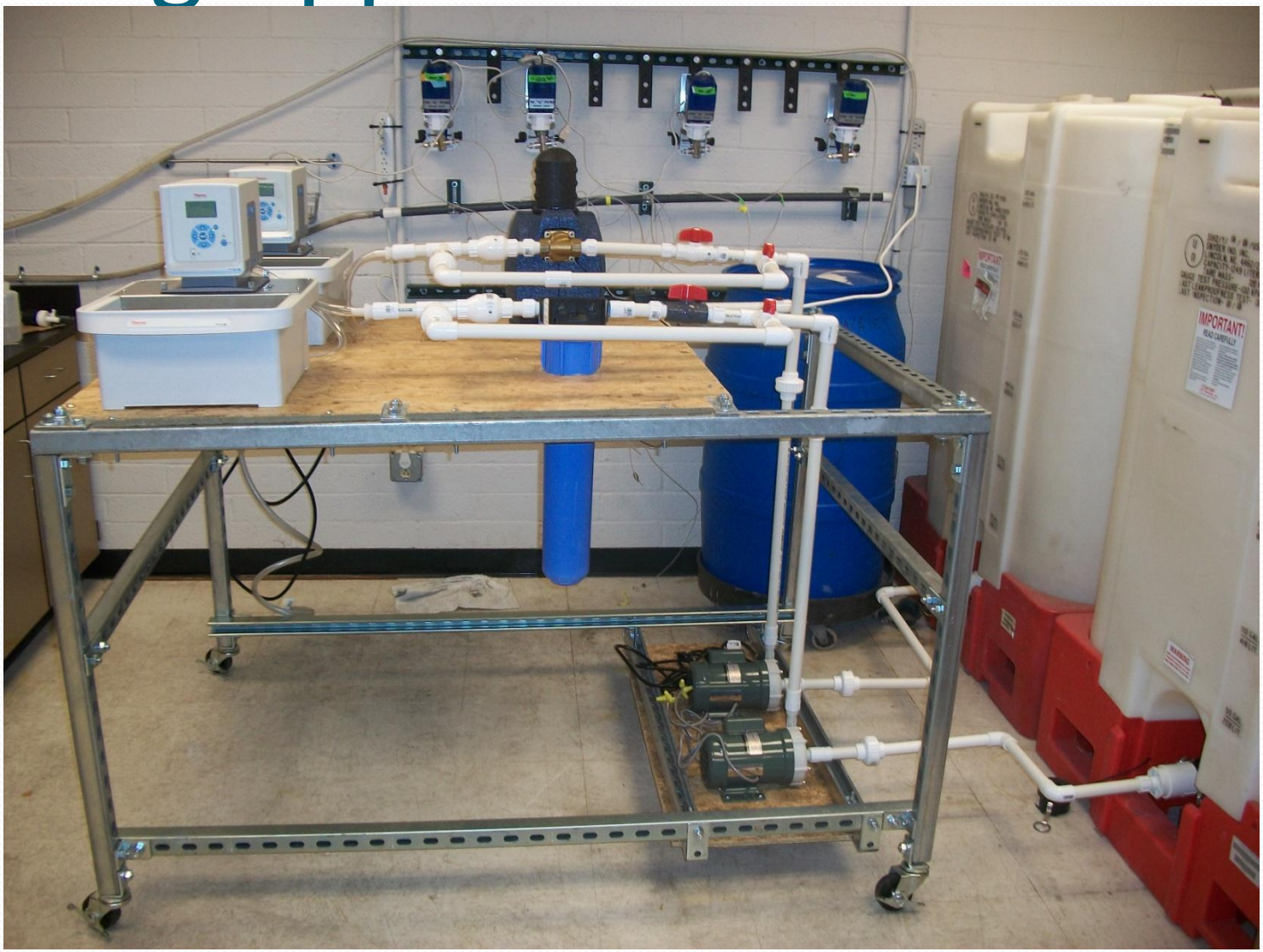
No backwash required

Filters sometimes sold with the technology

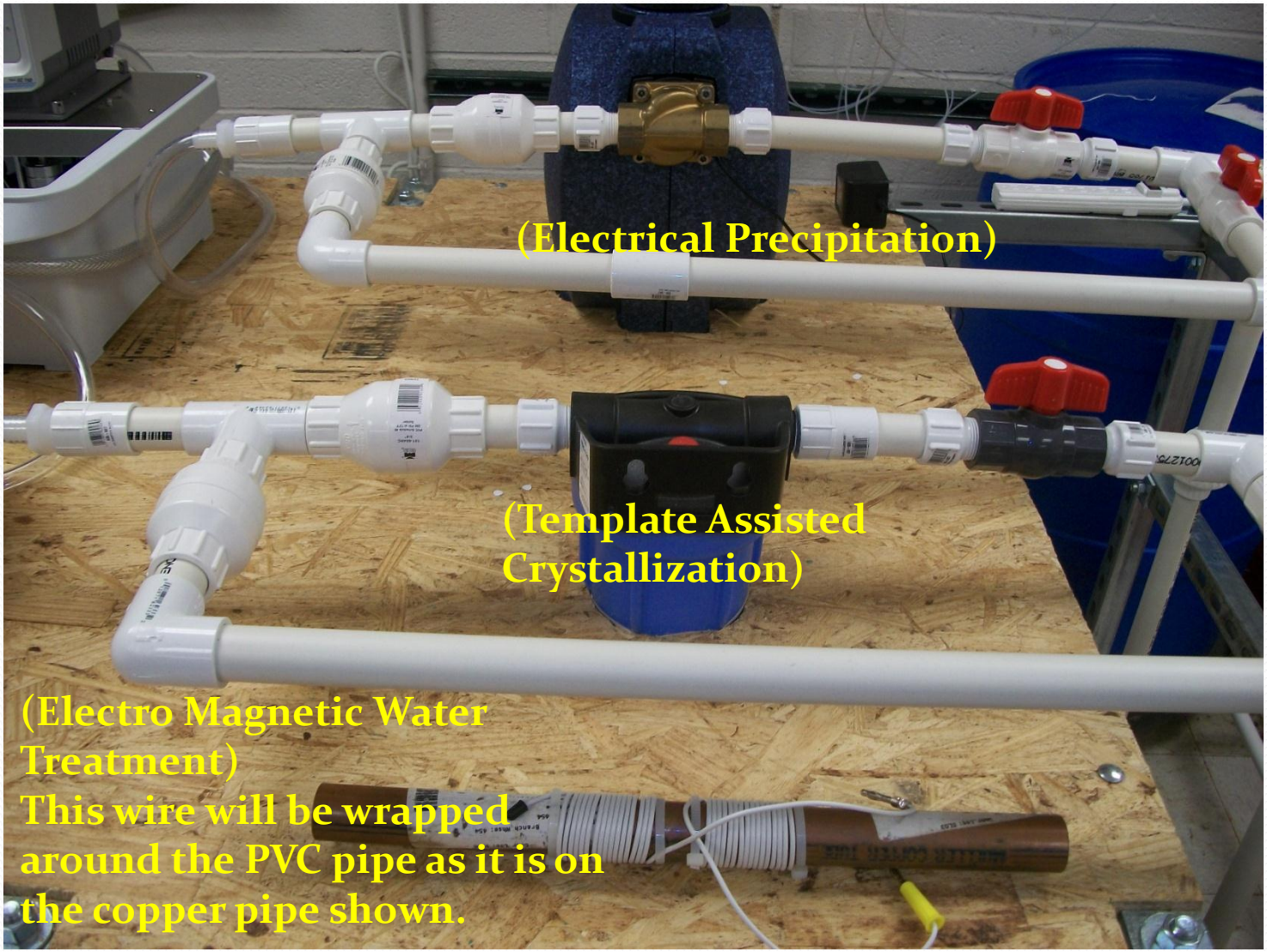
# Testing Methodology

- Protocol based on DVGW W512 test to assess control of scale formation
- Pump 130 L 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 Issues

- 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 an unrealistically low watt density. We used a watt density typical of an electric water heater.

# 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 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 to be Tested

- City of Tempe Tap water – Salt River (180 mg/l of hardness as $CaCO_3$)
- 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 (200-250 mg/L of hardness as $CaCO_3$)
- Santa Clara/San Jose Sub-basin Groundwater – Completed in California

# Schedule – Months of Testing at ASU

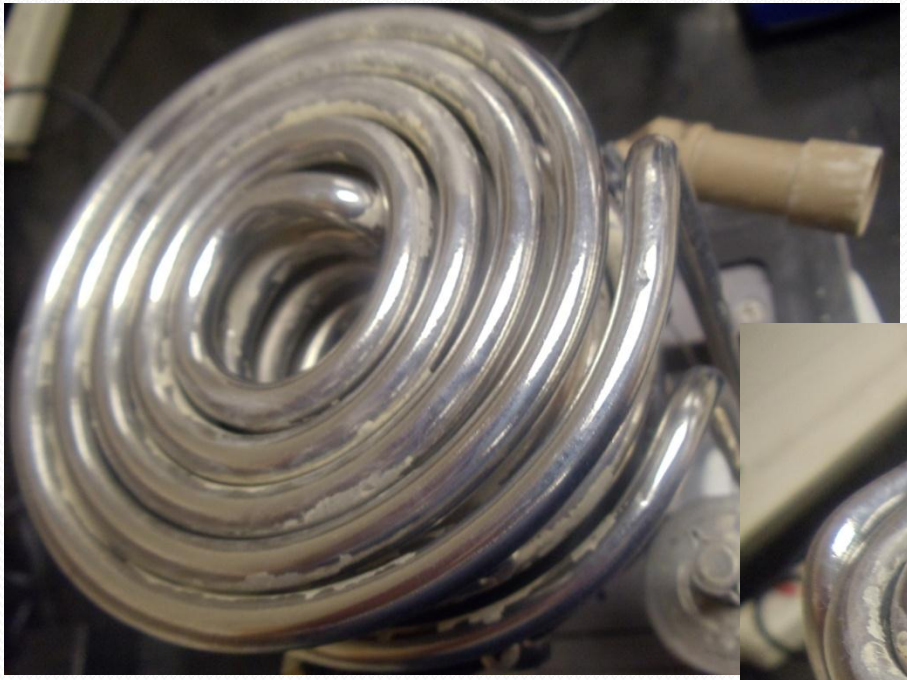
- Salt River Water – Three months

  First Two Runs - No Treatment and Ion exchange

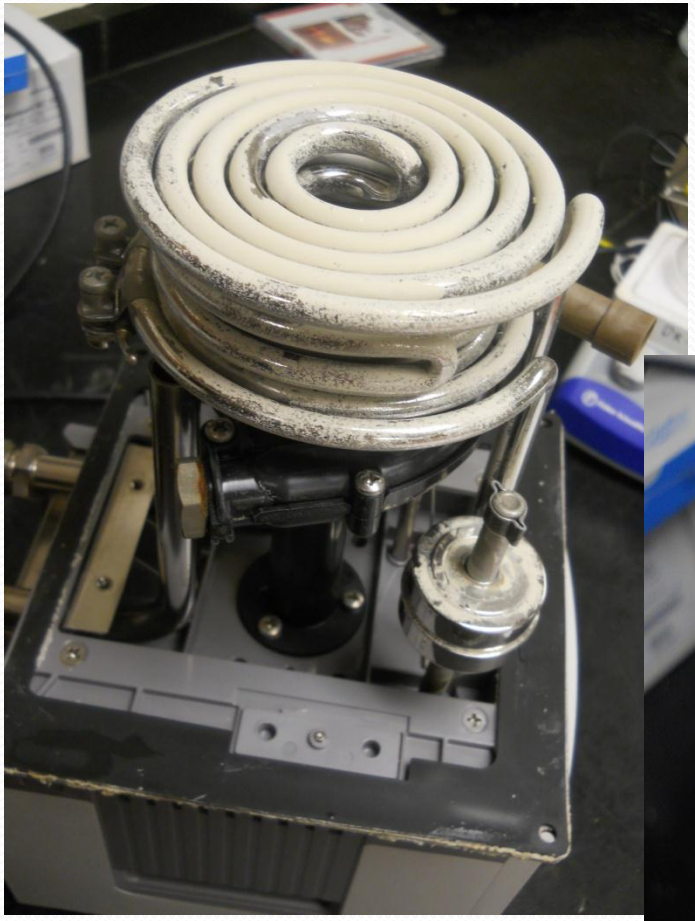
  Next Four Runs - Four Alternative Treatment Devices
- Colorado River water – Two months – Four Alternative Treatment Devices
- South Scottsdale Groundwater – Two months – Four Alternative Treatment Devices
- Salt River Water – Two Months – Repeat Tests at 60$^{o}$C

# RESULTS -Tempe Tap - Untreated

# Tempe Tap – Template Assisted Crystallization



# Tempe Tap – Electromagnetic



# Tempe Tap – Electrically Induced Precipitation

# Tempe Tap – Capacitive Deionization

Almost all scale measured was found in the bath.

# Results Summary

| Water Type | Treatment device used | Scale scraped off of heating element (g) | % Ca as $CaCO_3$ in scale formed | Ca formed in solid scale precipitate (g Ca as $CaCO_3$) | Scale from bath and heating element dissolved with HCl (g Ca as $CaCO_3$) | Total calcium formed during test (g Ca as $CaCO_3$) | Photo of heating element with scale |
|---|---|---|---|---|---|---|---|
| Tempe tap water | No Treatment | - | NA | 0.0 | 8.4 | 8.4 |  |
| | Template Assisted Crystallization | 0.0 | NA | 0.0 | 0.3 | 0.3 |  |
| | Electrically Induced Precipitation | 0.7 | 87.2 | 0.6 | 3.5 | 4.1 |  |
| | Electromagnetic | 1.4 | 87.2 | 1.3 | 3.6 | 4.9 |  |
| | Capacitive Deionization | 0.0 | NA | 0.0 | 1.4 | 1.4 |  |
| | Ion Exchange | | | | | | |

# Preliminary Results

- Template Assisted Crystallization worked best
- Capacitive Deionization worked well enough to pass DVGW test
- 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

# A rapid assessment test would be highly desirable

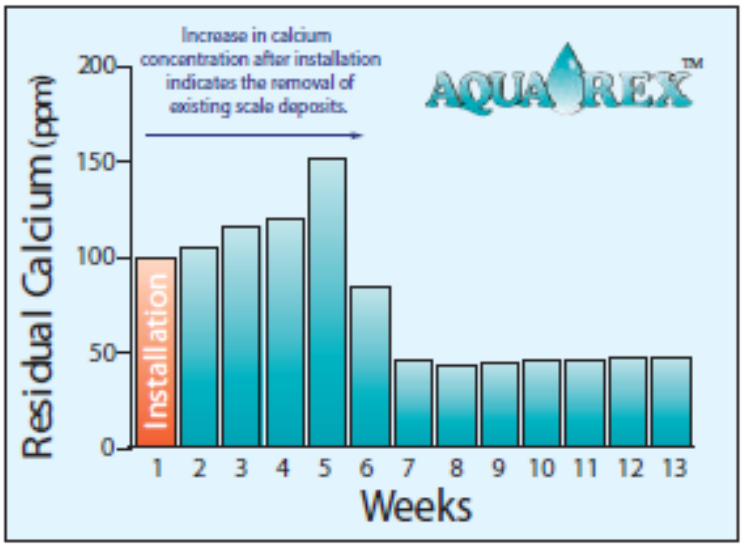
- Both Template Assisted Crystallization and Electromagnetic Devices might create microscopic forms of $CaCO_3$ that remain suspended
- Use this fact to develop a rapid assessment test
- Two possible methods
- Filtration to separate suspended $CaCO_3$
- Hach Kit – EDTA will only measure soluble Ca and Mg
- Surface Tension, X-ray diffraction, spectroscopy, etc.

# Results with Hach Kit using Electromagnetic Treatment

| Tempe Tap Water | Total Hardness | After Acidification |
|---|---|---|
| No Treatment | 163.2 | |
| After Electromagnetic Treatment | 123.2 | 156.8 |
| After Template Assisted Crystallization Treatment | 168 | 167 |

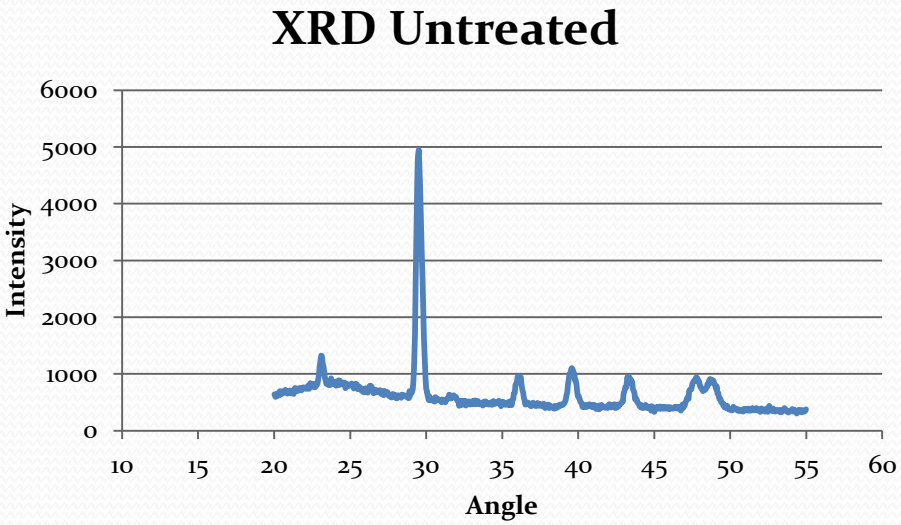
Langeleir Index with No Treatment = +0.24
Langeleir Index After EM Treatment = -0.08

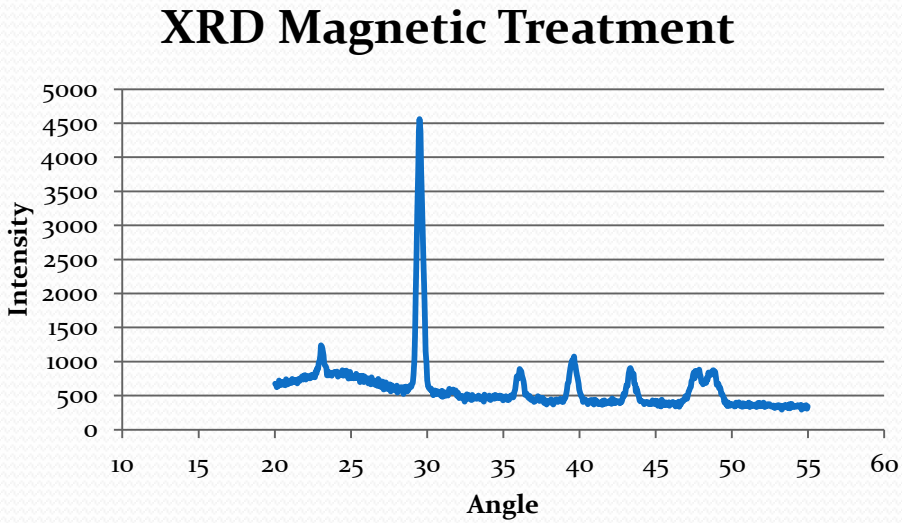
# IS THIS POSSIBLE?




In the tests a WK1 model was fitted in domestic premises located in a hard water area to treat the hot water system. It was sited on the cold supply pipe between the header tank and the water heater. Water was sampled weekly and double filtered through a 0.45 µm micro-fibre filter. The residual calcium concentration was measured using a Z8100 Hitachi Absorption Photometer.

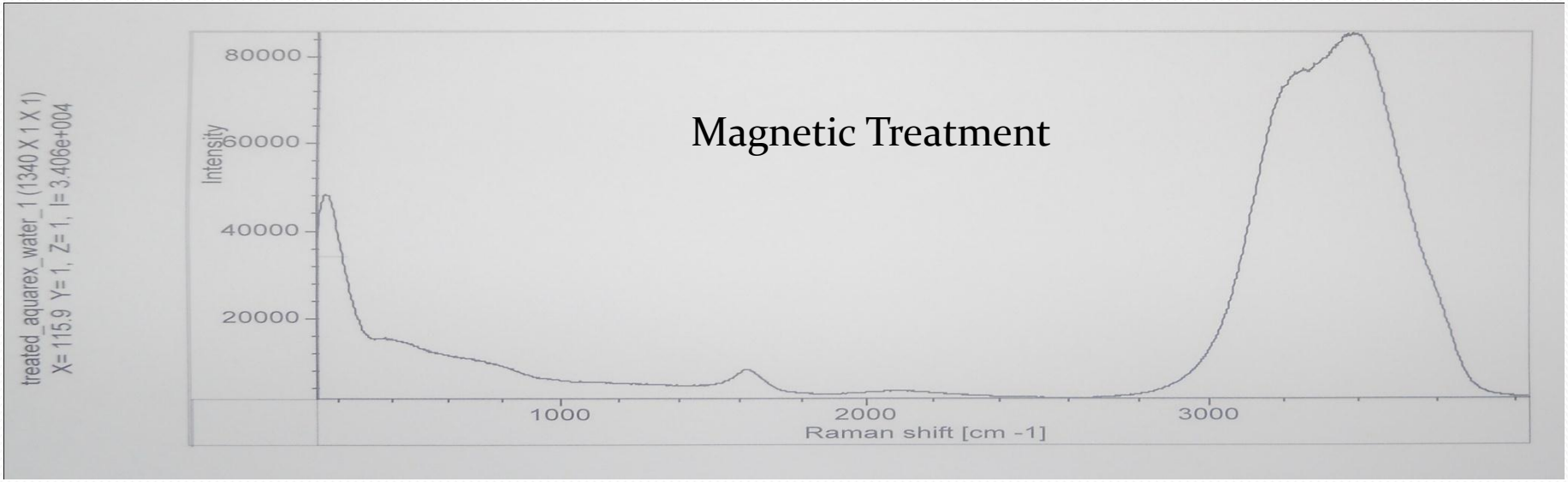
# X Ray Diffraction

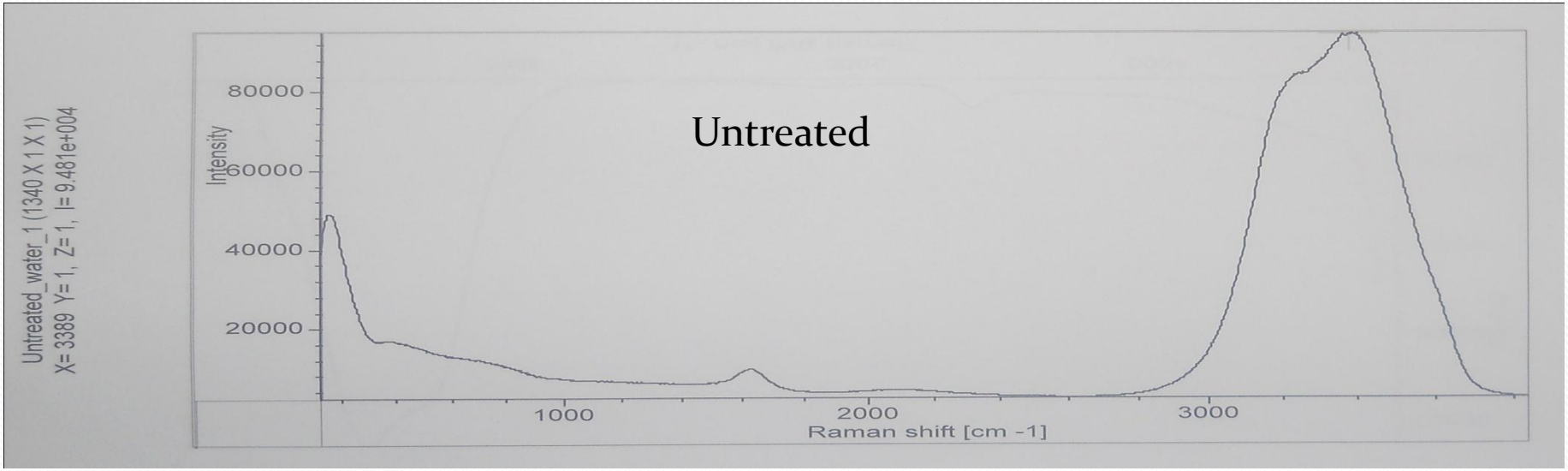



Both have calcite patterned peaks.

# RAMAN Spectroscopy




RAMAN Spectrum of water

# Acceptance??? – not up to Water Reuse Foundation or Researchers

- IAPMO is developing a standard protocol based on the DVGW – National Sanitation Foundation can then certify
- Industrial/Commercial applications are strong candidates – understand maintenance issues and desire cost savings
- Homeowners – depends on green movement and willingness to accept potential problems (Dissolved $CO_2$, etc.)