A Synergistic Combination of Advanced Separation and Chemical Scale Inhibitor Technologies for Efficient Use of Impaired Water as Cooling Water in Coal-Based Power Plants

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Outline

- Introduction
- Technical Approaches
- Task Plan
- Progresses to Date
- Next Steps

Nalco Company Overview

- Nalco Company is a leader in water treatment with more than 70,000 customers worldwide
- Three business units
  - Industrial and Institutional
  - Paper
  - Energy
- Nalco produces & supplies chemicals, equipment and service for a wide range of customers including power plants

Project Overview

- Participants
  - Nalco Company, LEAD
  - Argonne National Laboratory, via CRADA (Nalco-Argonne CRADA #C0600501)
- Duration
  - 41 months (March 31, 2006 to August 30, 2009)
- Goal
  - To minimize fresh water use by using impaired water for cooling
- Technology needs
  - Scale control technologies for impaired water in recirculating cooling water systems at high cycles of concentrations
- Approach
  - Synergistic combination of physical and chemical technologies
    - Separation processes to reduce the scaling potential
    - Scale inhibitors to extend the safe operating range

Task Plan

- Phase 1: Technical Targets and Proof of Concept (Years 1 & 2)
  - Task 1: Identify Limiting Factors for High Cycles and Quantify Technical Targets (Months 1-12)
  - Task 2: Develop High Stress Calcite and Silica Scale Control Chemistries (Months 1-18)
  - Task 3: Develop Advanced Membrane Separation Technologies and Processes (Months 2-18)
- Phase 2: Technology Development and Integration (Years 2 and 3)
  - Task 4: Develop Additional Novel Scale Control Chemistries (Months 19-30)
  - Task 5: Develop and Integrate Separation Processes (Months 19-30)

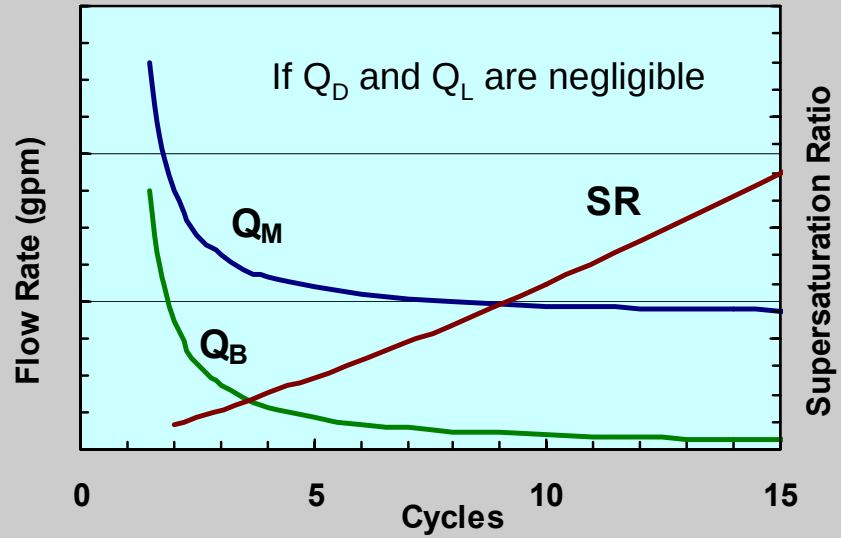
Task Plan (cont'd)

- Phase Three: Technology Validation (Years 3 and 4)
  - Task 6: Pilot Technology Demonstration (Months 30-41)
  - Task 7: Prepare Final Report (Months 40-41)

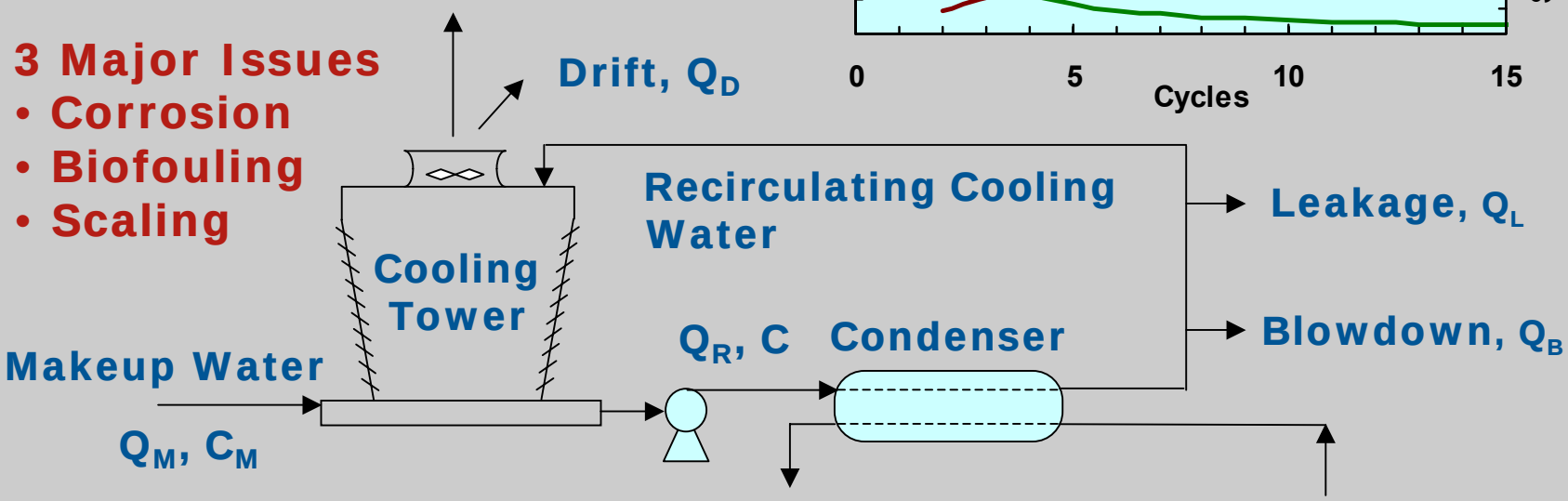
Open Re-circulating Cooling Water System

Cycles of concentration
$= 1 + Q_E / (Q_B + Q_D + Q_L)$

Scaling potential exists, if supersaturation ratio > 1



3 Major Issues
- Corrosion
- Biofouling
- Scaling

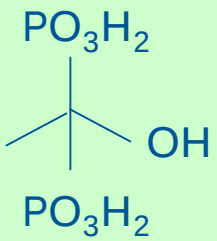


Q: Flow Rate
C: Concentration

Scale Inhibitors

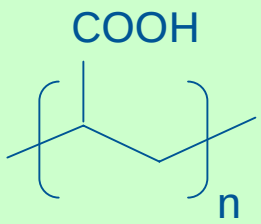
Chemistry

- Phosphonates



HEDP

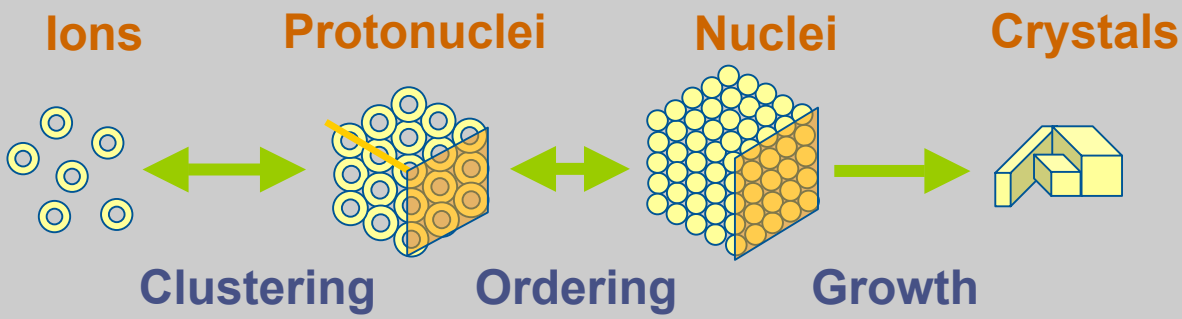
- Polymers



Polyacrylic Acid

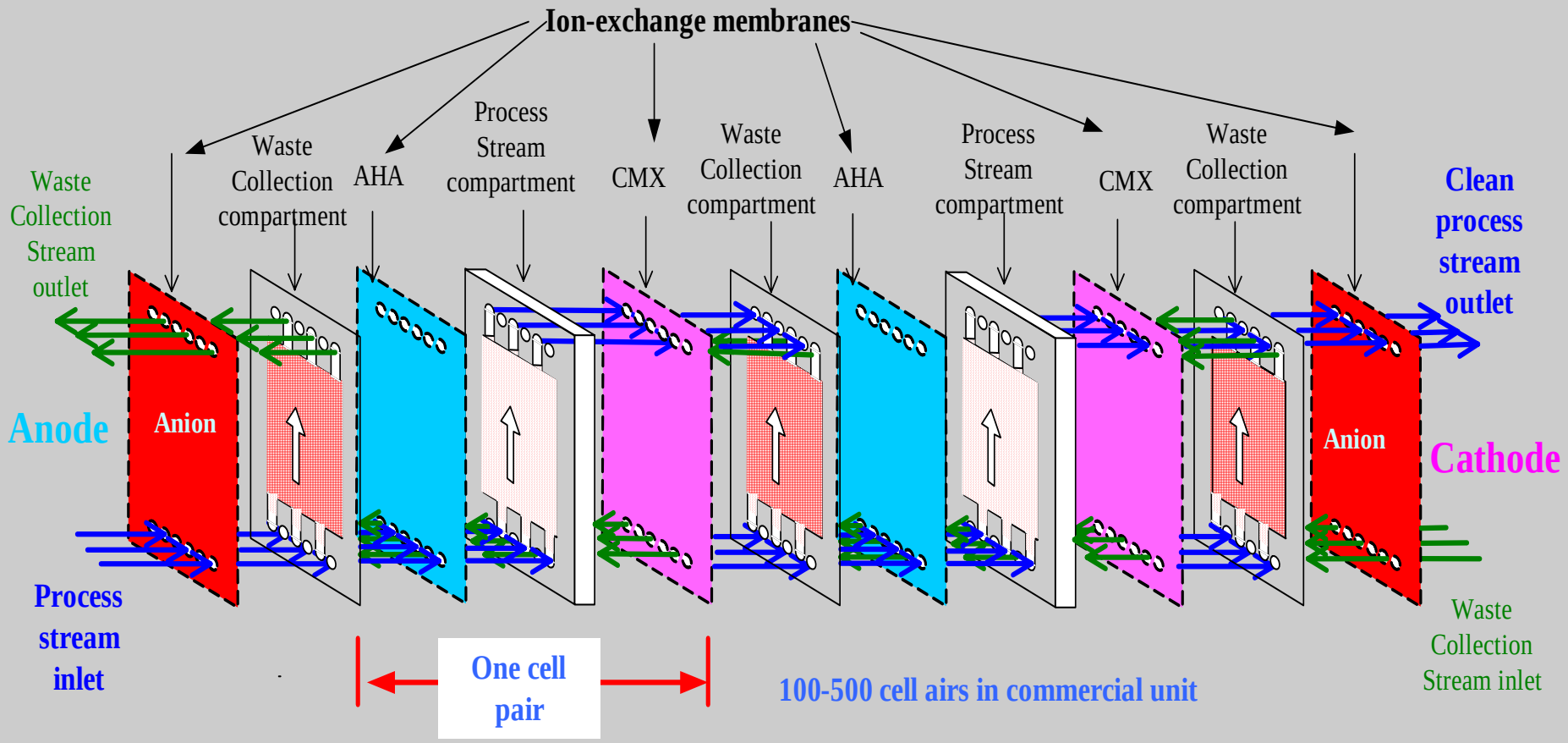
Mechanisms

- Threshold Inhibitors
  - Delay the ordering process
- Crystal Modifiers
  - Form irregular crystals that are less adhering
- Dispersants
  - Keep crystals suspended in water



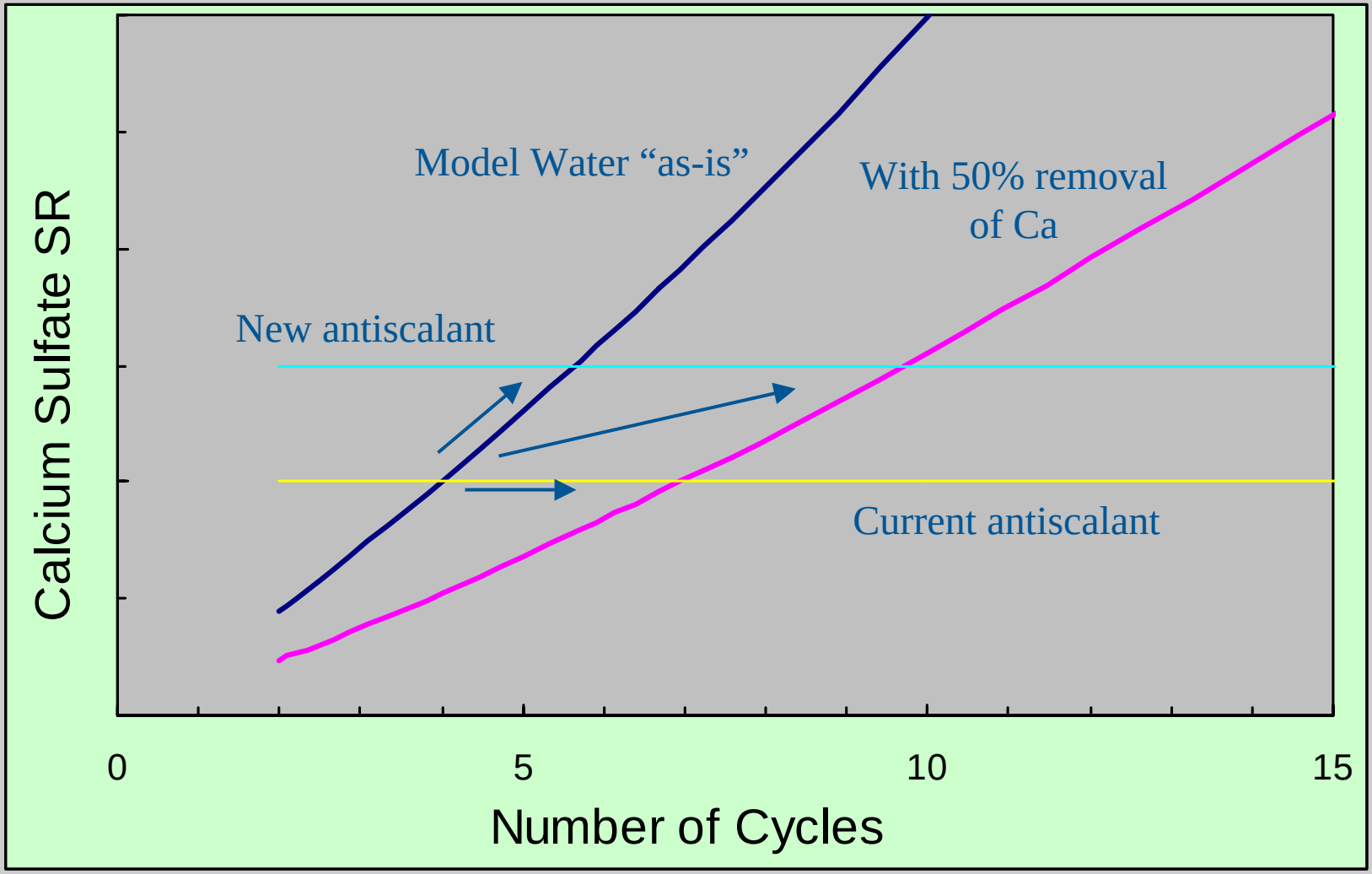
Stages of Crystallization

ED and RW-EDI Technologies



Synergy of Separations and Scale Inhibitors

Model Water: Agricultural Drainage Water in California (EPRI and CEC, 2003)



Task 1 Progress Update

- Reviewed Literature and existing Nalco data on characteristics of impaired waters.
  - Produced water
  - Municipal secondary effluent
- Additional target impaired waters were identified and samples collected for analysis
- Calculated of scaling limitations of impaired.

Typical Produced Water Characteristics

Reference	Tsai (1995)		Nalco	EPRI & CEC (2003)	EPRI (2004)	
Location	Site B	Site C	Gillette, WY	Central Valley, CA	McGrath, NM	Fairway, NM
Type		CBM	CBM	Oil Well	Mixed	CBM
pH	7.6	7.2	8.1	7.9	7.1	8.0
TDS, mg/L	8,000	14,700	4,000	3,879	12,714	12,236
Na, mg/L	2,640	6,200	870	982	4,149	3,620
Ca, mg/L	18.9	22.1	44	40	143	31.0
Ba, mg/L	10.1	27.2	1.5		3.1	25.1
Fe, mg/L	3.87	3.16	0.6		41	4.87
Cl, mg/L	18.9	1,920	25	920	6,298	2,018
SO4, mg/L	6.9	10.6	0	110	544	4.3
HCO3, mg/L	1,976	11,700	2,684	1,100	765	6,381
SiO2, mg/L			15	120	18.5	21.4

Typical Municipal Secondary Effluent Characteristics

Reference	Nalco			EPRI & CEC (2003)
Location	OCWD, CA	DDSD, CA	Naperville, IL	Bay Area, CA
pH	7.8	8.0	7.9	7.0
TDS, mg/L	940	1190	555	869
Na, mg/L	230	248.3	88.0	76
Ca, mg/L	82.0	52.1	64.0	76
Fe, mg/L	0.55	0.19	0.08	
Al, mg/L		0.4		
Cl, mg/L		290.5	120	102
SO4, mg/L		220.8	60	68
PO4, mg/L	2.5	0.6	2.0	6.0
HCO3, mg/L		305	171	1100
SiO2, mg/L	26.0		8.3	17

Scaling Limitations

- Common cycle-limiting species
  - Calcium carbonate
  - Silica/silicate
    - With co-presence of high silica
  - Calcium sulfate
    - ➢ Often due to sulfuric acid for pH control
  - Calcium phosphate (municipal effluent)
  - Iron and aluminum
- Challenges vary for each impaired water and power plant

Proposed Technical Strategy

Universal methodology to develop case-specific solutions

- Recognize and address interdependence of scaling/corrosion/biofouling
- Use model to select and control operating conditions, such as pH and cycles of concentration
- Address scale control and blowdown management simultaneously
- Use combination of different technologies for scale control, including scale inhibitors, separation technologies and cooling tower operations
  - Need a well-equipped technology tool box

Task 2 Progress Update

- Scale control chemistries for high stress calcite and silica control
- Silica/silicate
  - Laboratory screening of candidate chemistries completed
  - Selected promising candidate
  - Completed two field trials at Coal fired PP using the selected molecule
- Calcite/Calcium sulfate control
  - Candidate chemistries identified
  - Laboratory screening completed
  - Field trial completed at ZLD

Established the Limits of Chemical Treatment

Silica Scale

- Silica is often the limiting factor in impaired waters
- It is often encountered in both hot surfaces and cold surfaces
- Silica scales are tenacious, insulating, and difficult to remove.

- Silica deposition is caused by:
  - polymerization
  - precipitation with multi-valent ions
  - co-precipitation with other minerals
  - biological activity

Silica deposition processes occur simultaneously, and all must be controlled.

Calcium Carbonate

Different polymorphs are formed depending on the temperature, salinity and presence of multivalent ions in the brine

•Less soluble at higher temperature and higher pH

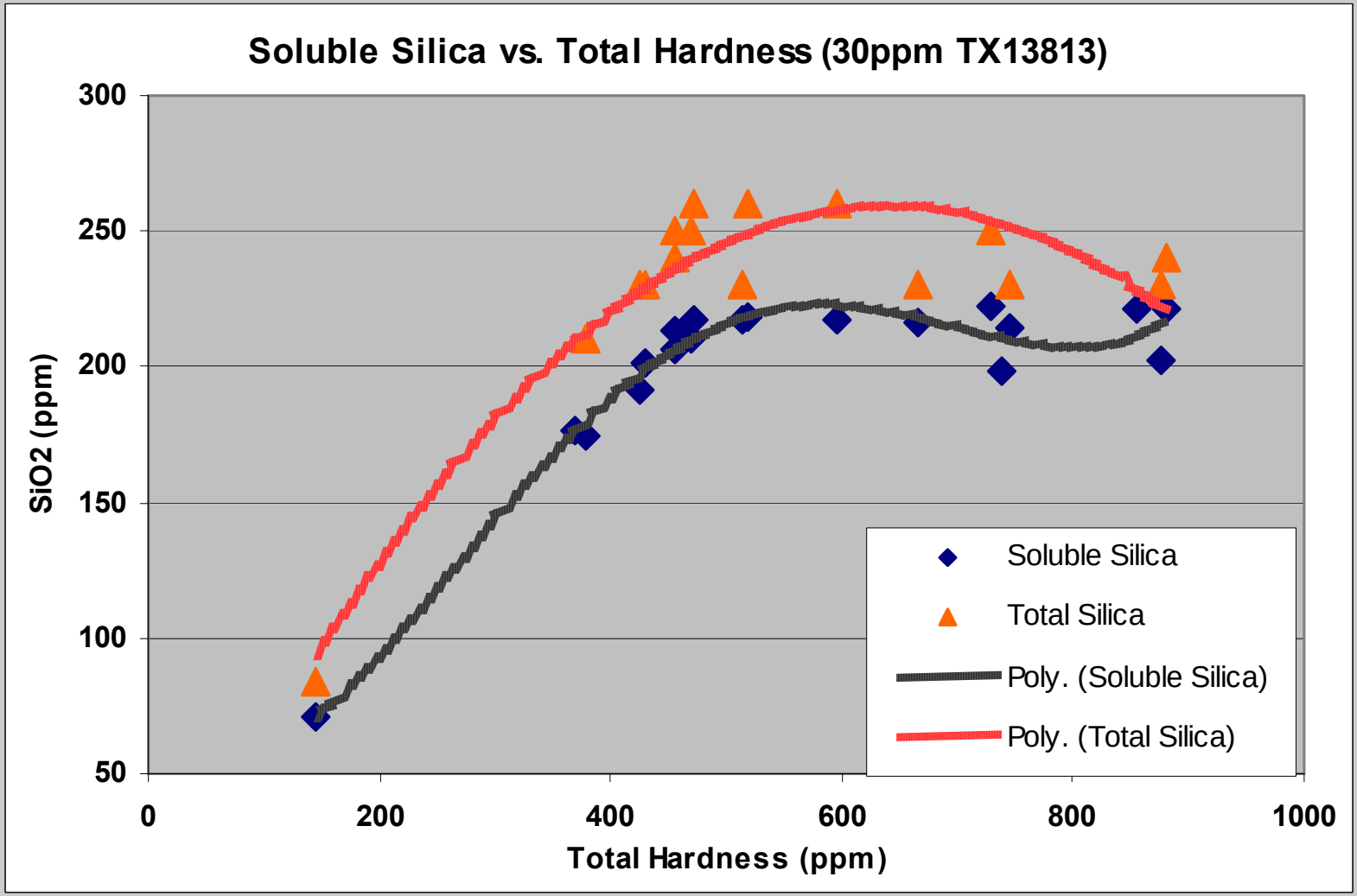
Can be controlled by either acid or scale inhibitor

Laboratory Study

Beaker Study

	Silica SiO_2 PPM	
Time (minutes)	No Inhibitor	20PPM Inhibitor
0	300	300
10	230	300
20	180	300
30	160	290
45	150	280

Laboratory Study



Phase 2 &3 Progress

Field Study

1. Coal Fired Western PP with ZLD
2. South Western Power Plant limited by Silica

Case Study 1

- Coal Fired with Total of >500 Megawatts electric output.
- There are multiple units each> 100MW generating capacity.
- The cooling towers operate at 7-8 cycles and is a ZLD facility with on site evaporative pond.
- The source of make up water (30-35 PPM as SiO_2) is a blend of River water and well water stored in Ponds.
- The towers have PVC Splash fill.

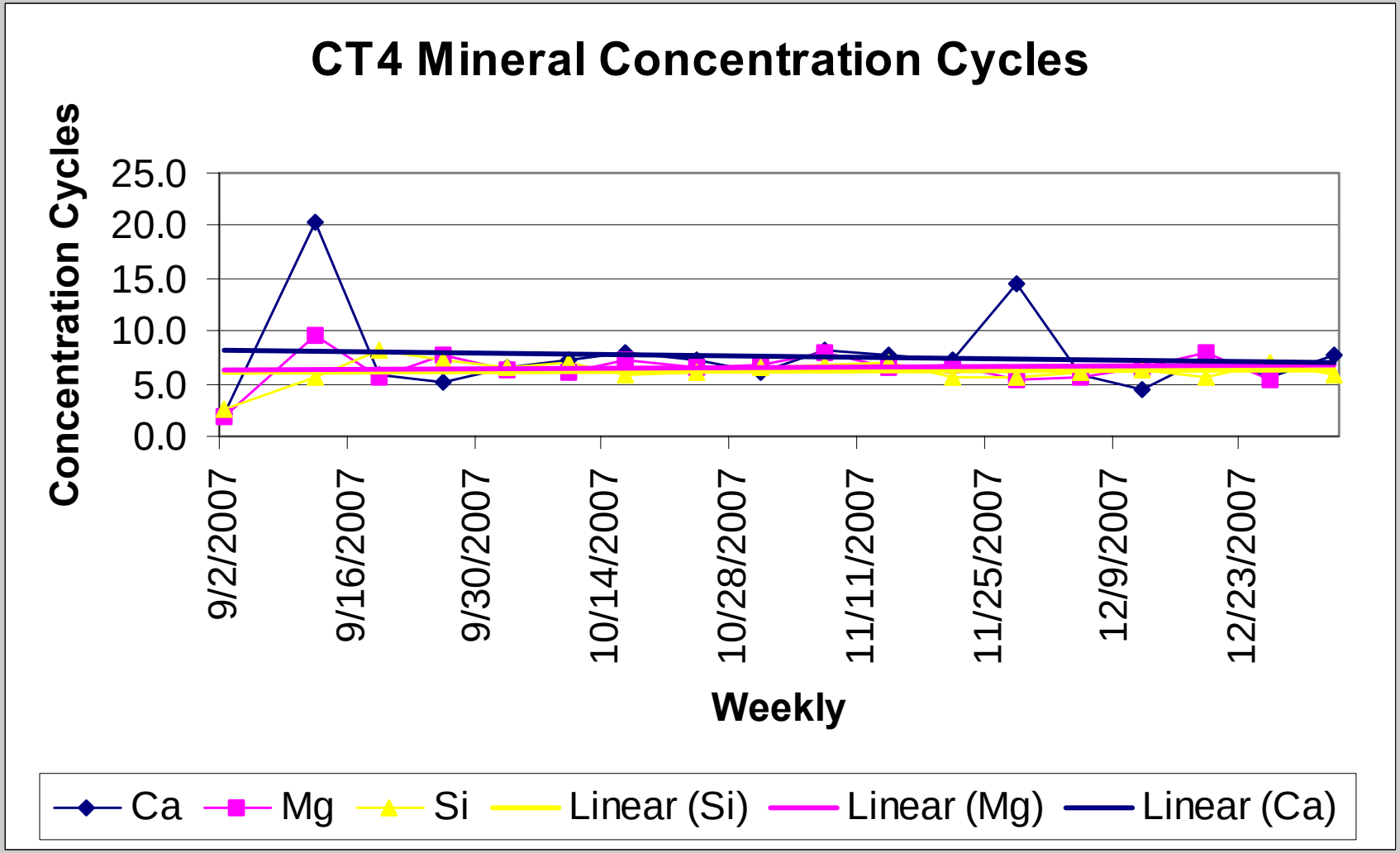
Chemical Treatment

3DT195	40 PPM (Tag control)
3DT199	5 PPM (slaved)
TX138813 (silica inhibitor)	20 PPM (Slaved)
Bleach	0.43 ppm FRH (ORP control)

Tower Chemistry

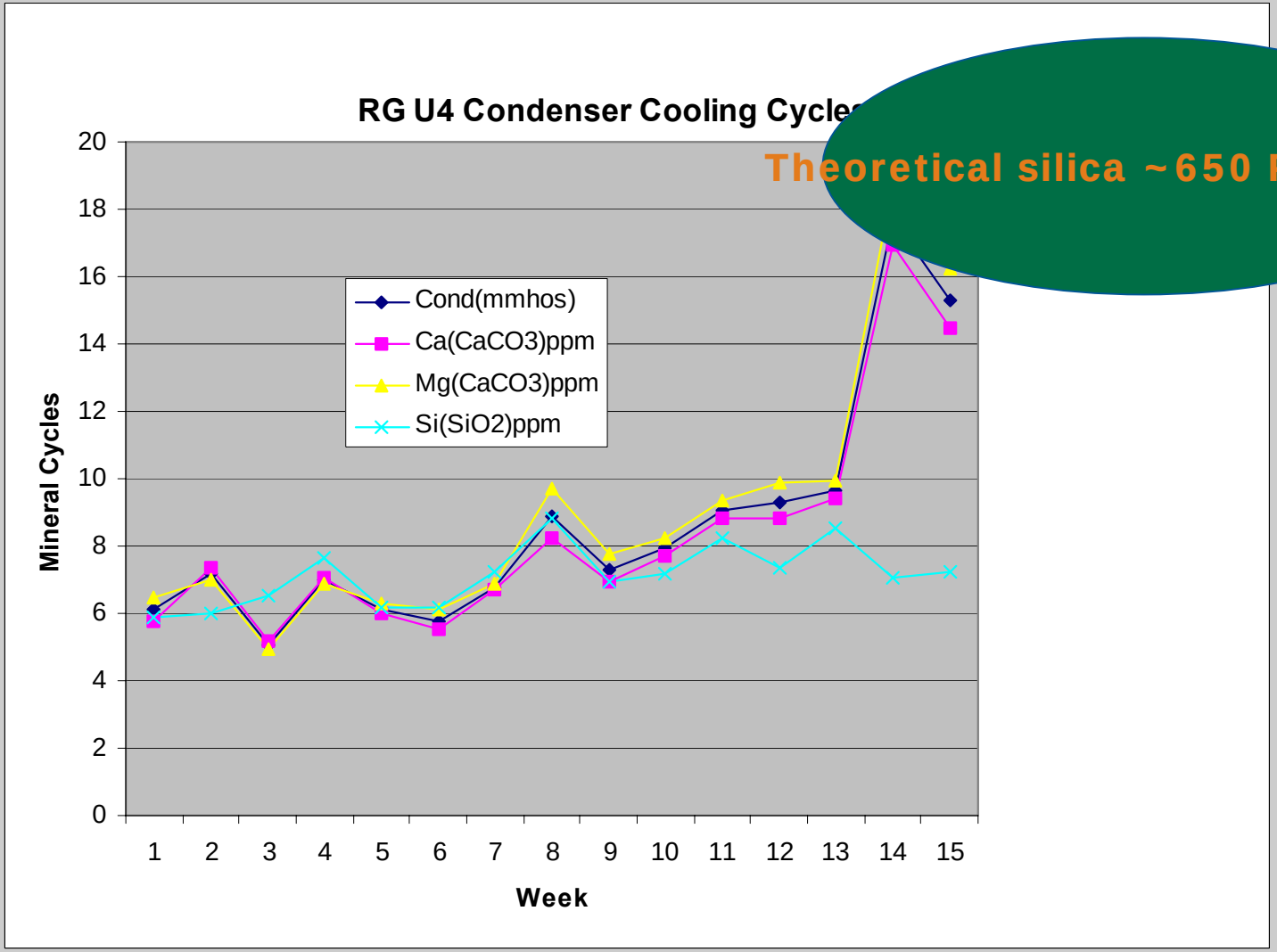
Tower Chemistry	Value	Unit
pH	7.6	Unitless
Calcium	378	ppm as Ca
M Alkalinity	71	ppm as CaCO3
Conductivity	6,860	µS/cm
Aluminum	0.0	ppm Al
Ammonia	0.0	ppm NH3
Chloride	494	ppm Cl
Iron	0.0	ppm as Fe
Magnesium	182	ppm Mg
Manganese	0.0	ppm Mn
Silica	224	ppm SiO2
Sulfate	2,544	ppm SO4
Turbidity	35	NTU

Unit 4 Cycles of Concentration



Upset Conditions(BD)

(Conductivity from 6200 to 18590 US/Cm)



Theoretical silica ~650 PPM as SiO_2

Heat Exchanger After the Upset

Performance of LL99B0
(Calcium carbonate Control)

Comparison of Inhibition at 300X Calcite Supersaturation, pH 9.0, Temperature 55 °C

Inhibitor	Active Dose PPM	% Inhibition
AMP	25	41
HMDTMP	25	55
PBTCA	25	57
HEDP-AMP-AA/AMPS Copolymer	23.4	60
LL99B0	25	100
PMA	25	56
AEC	25	62

Performance of LL99B0

Mixed calcium carbonate and calcium sulfate inhibition with LL99B0, pH 7.5 250 °C; SO4 1500 PPM

Inhibitor	Dose PPM	% Inhibition at various Calcium PPM			
		50	100	500	1000
PAA	5	100	100	60	0
	10	100	100	60	0
PMA	5	100	80	70	0
	10	100	80	60	0
LL99B0 & Polymer	5	100	100	100	72
	10	100	100	100	89

Western Coal Fired PP ZLD

>400 MW Net Coal Fired Power Generation station

Water Recirculating Rate varied between 100,000-200,000 GPM

Make up water source is river water

Automated Blow down based on conductivity and Calcium level at a rate of 280-312 GPM (average)

HTI ~ 168 hours; 11-12 cycles of concentration

High Efficiency Fill

Typical Tower Water Chemistry

Ion/parameter	PPM	Ion/parameter	PPM
pH	7.6-8.0	Sulfate	3600-4200
Conductivity (uS/Cm)	6300-6500	Sodium	650-725
Calcium	1600-1700	Silica	65-110
Magnesium	1000-1200	Total Phosphate	8.1-8.9
Alkalinity	70-90	O-Phosphate	5.1-5.7
Chloride	375-425	Turbidity (ntu)	2.1-2.3

Task 3 Progress Update

- Feasibility of membrane separation technologies
  - Electrodialysis and electrodeionization (Argonne lead)
- Task started when CRADA with Argonne was signed
- Key technical issues
  - Selectivity
  - Energy consumption
  - Flux
  - Scale control

Tasks 5.2 and 5.3 Membrane Separation Technology Feasibility Evaluation

1. Evaluation electrodialysis (ED) membrane separation to remove hardness from impaired water
   - Screen ion-exchange membrane
   - Evaluate energy cost for processing stream

2. Evaluation of Resin Wafer ElectroDeionIzation (RW-EDI) membrane separation to remove alkalinity and in-situ pH control for impaired water
   - Screen and optimize resin wafer
   - Optimize EDI stack configuration for pH-control and maximum alkalinity removal

3. Integration evaluation of EDI and heat-exchanger system

Compositions of Simulated Waters

Feed Compositions

Water #	1A	1B	2A	2B	3A	3B	
Water simulated	High Hardness Water	High Hardness Water	Produced Water (Gilette, WY)	Produced Water (Gilette, WY)	Produced Water (Fairway, NM)	Produced Water (Fairway, NM)	
Stream simulated	Make-up	Side Stream at 10 cycles with 50% Removal of Calcium and Magnesium at pH 7.5	Make-up	Side Stream at 10 cycles and pH 8.0	Make-up	Side Stream at 10 cycles and pH 8.0	Molecular Weight, g/mole
Application #	1	1	2	2	2	2	
Analyses							
Calcium, mg/L as Ca	70.0	350.0	0.0	0.0	0.0	0.0	40
Magnesium, mg/L as Mg	19.0	95.0	0.0	0.0	0.0	0.0	24.3
Sodium, mg/L as Na	275.0	2750.0	1045.0	1345.0	3800.0	15500.0	23.0
Chloride, mg/L as Cl	390.0	3045.0	50.0	500.0	2000.0	20000.0	35.5
Sulfate, mg/L as SO4	192.0	2739.0	0.0	0.0	0.0	0.0	96
Bicarbonate, mg/L as HCO3	121.5	121.7	2655.0	2662.9	6405.3	6395.2	61
Carbonate, mg/L as CO3	0.3	0.5	22.5	24.2	82.9	168.4	60
Carbon dioxide, mg/L as CO2	4.7	3.6	30.5	29.8	61.5	44.7	44
Total dissolved solids, mg/L	1079.0	9099.0	3785.1	4505.1	12285.1	42065.1	
pH	7.5	7.5	8.0	8.0	8.0	8.0	
Temperature (oC)	25.0	25.0	25.0	25.0	25.0	25.0	

Applications
#1: Preferential removal of calcium over sodium using ED
#2: Removal of alkalinity without acid using WSED or EDI

Cations (mN)	17.02	144.88	45.43	58.48	165.22	673.91
Anions (mN)	16.99	144.85	45.68	58.55	164.11	673.83
NaCl equivalent (mg/l)	995	8475	2665	3423	9633	39422

Results of Feasibility Evaluation

Hardness Removal from 10X blowdown and makeup water

Hardness is preferentially removed compared to mono-valent ions

Process Range Salt content (inlet - effluent)	Salt Removal (%)	Power consumption (kWh/100 gal water)
9000 ppm to <10 ppm	> 99%	3.0
1000 ppm to < 15 ppm	>98%	0.45

Results of Feasibility Evaluation

Alkalinity Removal & pH Adjust

Process Range	Salt Removal	Power consumption	effluent pH
Salt content (inlet - effluent)	(%)	(kWh/100 gal water)	
4000 ppm to <40 ppm	> 99%	3-5	5 5-7.0.
500 ppm to < 40 ppm	>94%	1-2	5.5-7.0

Assessment of Pre- and Post-Treatment of Water Reused for Heat-Exchanger

Impaired Water	gal/day	**100,000**	
		Blow-down water	Make-up water
Process Concentration (inlet - effluent)		5000 - 500 ppm	500 - 50 ppm
Power consumption	wkh/100gal	5.00	1.00
Effluent pH		6.0-7.0	5.5-6.5
Estimated Capital cost		$ 150,000	$ 500,000
Electricity	KW	300	60