FINAL REPORT

March 31, 2006 to August 30, 2010

DOE Award Number: DE-FC26-06NT42721

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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Report Issued December 2010

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EXECUTIVE SUMMARY

Nalco Company is partnering with Argonne National Laboratory (ANL) in this project to jointly develop advanced scale control technologies that will provide cost-effective solutions for coal-based power plants to operate recirculating cooling water systems at high cycles using impaired waters. The overall approach is to use combinations of novel membrane separations and scale inhibitor technologies that will work synergistically, with membrane separations reducing the scaling potential of the cooling water and scale inhibitors extending the safe operating range of the cooling water system.

The project started on March 31, 2006 and ended in August 30, 2010. The project was a multi-year, multi-phase project with laboratory research and development as well as a small pilot-scale field demonstration. In Phase 1 (Technical Targets and Proof of Concept), the objectives were to establish quantitative technical targets and develop calcite and silica scale inhibitor chemistries for high stress conditions. Additional Phase I work included bench-scale testing to determine the feasibility of two membrane separation technologies (electrodialysis ED and electrodeionization EDI) for scale minimization. In Phase 2 (Technology Development and Integration), the objectives were to develop additional novel scale inhibitor chemistries, develop selected separation processes, and optimize the integration of the technology components at the laboratory scale. Phase 3 (Technology Validation) validated the integrated system's performance with a pilot-scale demonstration.

During Phase 1, Initial evaluations of impaired water characteristics focused on produced waters and reclaimed municipal wastewater effluents. Literature and new data were collected and evaluated. Characteristics of produced waters vary significantly from one site to another, whereas reclaimed municipal wastewater effluents have relatively more uniform characteristics. Assessment to date confirmed that calcite and silica/silicate are two common potential cycle-limiting minerals for using impaired waters. For produced waters, barium sulfate and calcium sulfate are two additional potential cycle-limiting minerals. For reclaimed municipal wastewater effluents, calcium phosphate scaling can be an issue, especially in the co-presence of high silica. Computational assessment, using a vast amount of Nalco's field data from coal fired power plants, showed that the limited use and reuse of impaired waters is due to the formation of deposit caused by the presence of iron, high hardness, high silica and high alkalinity in the water. Appropriate and cost-effective inhibitors were identified and developed – LL99B0 for calcite and gypsum inhibition and TX-15060 for silica inhibition. Nalco's existing dispersants HSP-1 and HSP-2 has excellent efficacy for dispersing Fe and Mn. ED and EDI were bench-scale tested by the CRADA partner Argonne National Laboratory for hardness, alkalinity and silica removal from synthetic make-up water and then cycled cooling water. Both systems showed low power consumption and 98-99% salt removal, however, the EDI system required 25-30% less power for silica removal.

For Phase 2, the EDI system's performance was optimized and the length of time between clean-in-place (CIP) increased by varying the wafer composition and membrane configuration. The enhanced EDI system could remove 88% of the hardness and 99% of the alkalinity with a processing flux of 19.2 gal/hr/m^2 and a power consumption of 0.54 kWh/100 gal water.

Bench tests to screen alternative silica/silicate scale inhibitor chemistries have begun. The silica/silicate control approaches using chemical inhibitors include inhibition of silicic acid polymerization and dispersion of silica/silicate crystals. Tests were conducted with an initial silica concentration of 290 -300 mg/L as SiO_2 at pH 7 and room temperature. A proprietary new chemistry was found to be promising, compared with a current commercial product commonly used for silica/silicate control. Additional pilot cooling tower testing confirmed the bench study. We also developed a molecule to inhibit calcium carbonate precipitation and calcium sulfate precipitation at high supersaturations.

During Phase 3, a long-term test of the EDI system and scale inhibitors was done at Nalco's cooling tower water testing facility, producing 850 gallons of high purity water (90+% salt removal) at a rate of 220 L/day. The EDI system's performance was stable when the salt concentration in the concentrate compartment (i.e. the EDI waste stream) was controlled and a CIP was done after every 48 hours of operation time. A combination of EDI and scale inhibitors completely eliminated blowdown discharge from the Pilot cooling Tower. The only water-consumption came from evaporation, CIP and EDI concentrate. Silica Inhibitor was evaluated in the field at a western coal fired power plant. Pilot cooling tower runs were successfully completed by partially removing scaling ions (carbonate, hardness, and silica) and controlling fouling by using low level of scale inhibitors.

PROJECT DESCRIPTION AND OBJECTIVES:

Water is essential to thermoelectric power plants, used primarily for cooling. Using impaired water in place of fresh water is a potentially attractive solution to the problems of water scarcity and competing demands. As the population increases, good fresh quality water is much more needed for human use including growing food. Tertiary sewage treated water has been successfully used in many industrial applications. The use of impaired water is currently not very practical and cost effective, as the inferior water quality results in additional treatment requirements to address the high propensities of scaling, corrosion, and biofouling and to avoid adverse impacts to the environment. Depending on the impairment the treatment cost is prohibitively high because 1) the current separation technologies are inefficient, and 2) the scaling potential of the impaired waters is generally high and severely limits the number of cycles that can be achieved with current scale control technologies. Scale inhibitors alone can only control deposit up to certain number of cycles of concentration; beyond their maximum limit it does not matter how much inhibitor is added. In these situations the only way to improve water reuse is to remove impairment either completely or partially (Figure1). Operating at low cycles reduces water utilization efficiency and greatly increases the volume of blowdown wastewater, resulting in unacceptable high costs and a significant environmental impact. In this figure, the yellow line represents the scale inhibitors only using existing commercial scale inhibitors while the teak color line represents the target for new scale inhibitor. The dark blue line represents model water as is while the magenta (red) color represents with at least 50% calcium hardness removed.

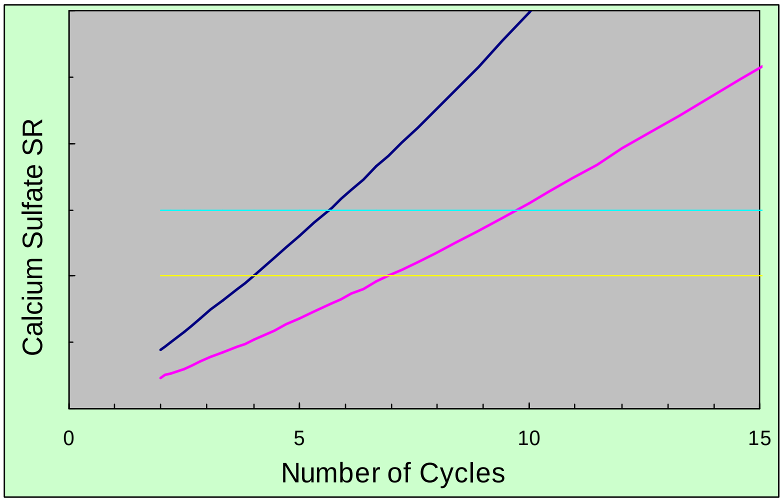


Figure1. Synergy of Ion Separations and Scale Inhibitors

Nalco Company is partnering with Argonne National Laboratory (ANL) in this project to jointly develop advanced scale control technologies that will provide cost-effective solutions for coal-based power plants to operate recirculating cooling water systems at high cycles using impaired waters. This will reduce the amount of make-up water required and the volume of blowdown generated, resulting in lower treatment cost and less environmental impact. The overall approach is to use synergistic combinations of physical and chemical technologies. More specifically, the project team will develop novel membrane separations and scale inhibitor technologies that will work synergistically, with membrane separations reducing the scaling potential of the cooling water and scale inhibitors extending the safe operating range of the cooling water system. This approach has not been possible to date because the technical risks involved in integrating these technologies have not been addressed. In this project, Nalco and ANL will develop the technology, knowledge, and strategies for optimum removal and management of scale-forming precursors. The project team will develop membrane separation technologies that are efficient, economical and compatible with scale inhibitors. The new scale inhibitor chemistries developed in this work will handle the higher stress scaling conditions as well as new types of scales from impaired water.

This is a multi-year, multi-phase project with laboratory research and development and small pilot scale field demonstration. In Phase 1, the objectives are to establish quantitative technical targets, develop calcite and silica scale inhibitor chemistries for high stress conditions, and determine the feasibility of various membrane separation technologies to minimize scaling. In Phase 2, the objectives are to develop additional novel scale inhibitor chemistries, develop selected separation processes, and optimize the compatibility of technology components at the laboratory scale. In Phase 3, the objective is to pilot the integrated technologies using selected model sites to validate the performance.

Technical Background and Approach:

Identify Limiting Factors for High Cycles and Quantify Technical Targets:

Potential sources of impaired waters were identified based on literature and industry information provided by Nalco's Power business unit. As the first step to determine the cycle-limiting factors of the impaired waters, the characteristics of various impaired waters are collected and evaluated. There are several sources of water that are used for cooling water application

- Ground water
- Surface water
- Tertiary sewage treated water (municipal waste water)
- Produced water
- Sea water/brackish water

General impairment with ground water in addition to hardness, alkalinity, and silica is the presence of iron and manganese. Surface water contains high suspended solids and many times colloidal silica in addition to dissolved silica and other ions mentioned in the ground water. Surface water, however, very rarely contain iron and manganese. The challenges with municipal waters are the presence of variable phosphate, ammonia and biological material. Produced water is not used very commonly for cooling tower. There has been a recent trend in the use of sea or brackish water being used in power plants in coastal areas. The impairment of these waters is due to the corrosive nature, which is overcome by using corrosive resistant metallurgy. Cooling towers using brackish or sea water are generally run at lower cycles due to abundance resource and easy discharge without impacting the environment. In this study we focused on high hardness, high alkalinity, and high silica waters and in general high total dissolved solids (TDS).

Nalco has developed a software tool (similar software tools can also be found in public and private domains) which uses thermodynamic calculations to determine the potential for scale formations for several minerals.

Development of High Stress Calcite and Silica Scale Control Chemistries:

Scale formation in cooling water systems occurs when mineral salts precipitate from the water phase because the solubility of the particular mineral has been exceeded (i.e., the water is supersaturated with the mineral). Supersaturation of any mineral is defined by the following relations,

Supersaturation = Activity product of scale forming ions/ Ks_p

Where, Ks_p is the thermodynamic equilibrium solubility constant of the mineral.
The process of scale formation from a supersaturated solution involves a series of steps, including nucleation, crystal growth and deposition on the heat exchangers. Chemical scale inhibitors (also known as antiscalants) control scale formation by a variety of mechanisms: threshold inhibition, crystal modification, sequestration, or dispersion. In terms of their chemical nature, scale inhibitors include inorganic polyphosphates (e.g., hexametaphosphate), organophosphonates (e.g., 1-hydroxyethylidene-1, 1-diphosphonic acid) and polymers (e.g., polyacrylate).

Antiscalants for calcite (calcium carbonate) and silica/silicate scale control are currently available. However, for high stress conditions (at high supersaturation ratios) these antiscalants are either ineffective or uneconomical. In this task, new scale inhibitor chemistries (including new molecules, polymers, and formulations) are being evaluated to develop new antiscalants that will be superior to existing antiscalants, in terms of cost and performance, in high stress conditions. The evaluations are performed initially in bench tests and, subsequently, in the pilot cooling towers.

The term silica is often used loosely to include both silica and silicates, which are, in fact, two distinct families of silicon-containing compounds. Silica refers to SiO_2, including the crystalline quartz and the non-crystalline amorphous silica, resulting from polymerization of silicic acid, H_2SiO_3. Silicates refer to the compounds formed by reacting ionized silicic acid with metals, such as calcium (Ca), magnesium (Mg), aluminum (Al), iron (Fe), zinc (Zn), etc. It is also very common for silica/silicates to coprecipitate on suspended solids or other precipitating minerals. The solubility of silica is approximately constant in the pH range of 6 to 8 and increases at pH 8.5 and higher. The solubility of silicates follows the opposite trend, and silicate precipitation generally occurs only at pH > 8.5. Silica/silicate control using chemical inhibitors include inhibition of silicic acid polymerization and dispersion of silica/silicate crystals. Amorphous silica solubility increases with increasing temperature while the solubility of silicates decreases with increasing temperature. Most of the time in cooling towers amorphous silica is deposited on the high efficiency fill and silicates are found on the heat exchangers surface in systems with moderately low silica levels. On the carbon steel heat exchanger surface due to the presence of hydroxyl groups, silica can directly deposit as silicates or even monomeric silica.

Calcium carbonate precipitation is directly a function of hardness, carbonate alkalinity, temperature, TDS and pH. Most of the time calcium carbonate precipitation is controlled by adjusting the pH of the recirculating water. There are several draw back to control calcium carbonate precipitation.

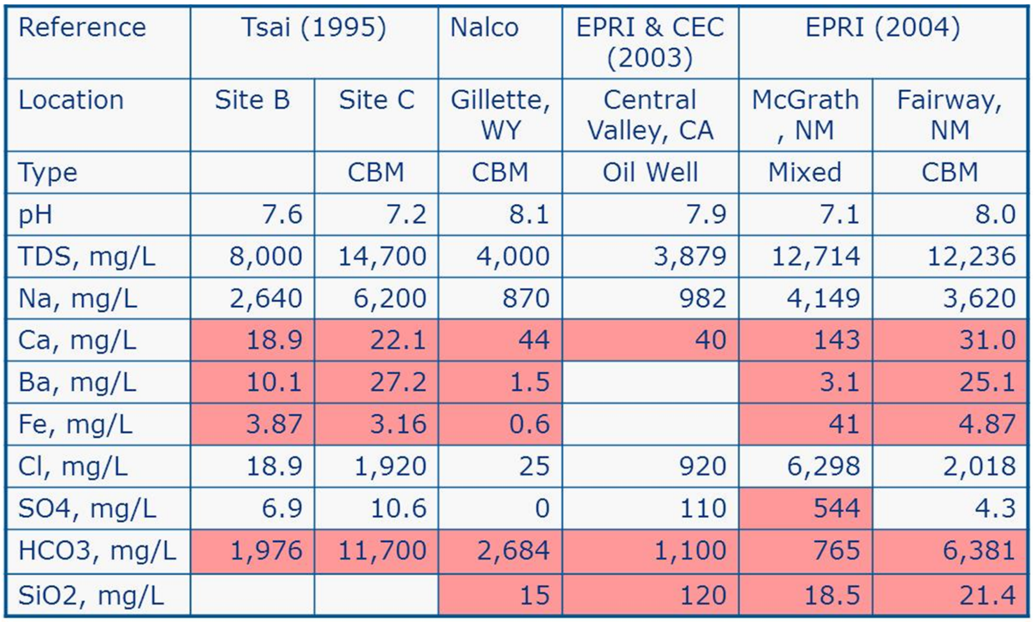
- Corrosion
- Other potential scales such as calcium and barium sulfate (if sulfuric acid is used for pH control)
- CO2 emission as a result of carbonate alkalinity neutralization.
- Cost

Solubility of calcium carbonate is inversely proportional to temperature and thus is a very common scale on the heat exchangers. Scale inhibitors have been used but largely in conjunction with pH adjustment for high cycles of concentration or high alkalinity waters.

Results and Discussion

Task 1. Identify Limiting Factors for High Cycles and Quantify Technical Targets:
Initial evaluations of impaired water characteristics focused on produced waters and reclaimed municipal wastewater effluents. Characteristics of produced waters have been reported in earlier work by others [1-3]. Table 1 shows that produced water characteristics can vary significantly from site to site, with respect to the total dissolved solids and the ion profile. Two common potential cycle-limiting minerals are calcium carbonate and calcium sulfate. These waters often contain very high levels of bicarbonate (HCO_3^-) ions and present unique challenges in calcium carbonate scale control. If one uses sulfuric acid addition to control the cooling water pH to control calcium carbonate scaling, the high levels of bicarbonate can result in a high consumption of sulfuric acid and, in turn, a risk for calcium sulfate and barium sulfate (if barium is present in the water even at very small amounts-0.5 -1.0 mg/L) scaling. Reduction in carbonate alkalinity by addition of sulfuric acid is also responsible for adding to the greenhouse gasses by emitting 0.73 ton of carbon dioxide for every ton of carbonate alkalinity reduced with sulfuric acid. Silica/silicate scaling is also a potential cycle-limiting factor, especially for produced waters from the western region. High levels of iron are also found in some produced waters (as high as 41 mg/L at the McGrath, New Mexico site), and present significant challenges.

Table 1.Characteristcs of produced water



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

Compared with produced waters, characteristics of reclaimed municipal wastewater effluents, as shown in Table 2, are more uniform from various sites. The total dissolved solids level varies from 500 to slightly over 1000 mg/L. Again, calcium carbonate is a common potential cycle-limiting factor, and silica/silicate is an issue for the western region. The concentration of phosphate in some reclaimed municipal effluents is high enough to potentially cause calcium phosphate scaling, and this can be a challenging issue, especially if silica is also present at high concentrations. The presence of iron and aluminum, due to their uses as treatment additives in upstream treatment processes, also present potential iron and aluminum fouling issues. However, the extent of potential iron and aluminum fouling appears to be controllable with current cooling water treatment technologies.

Table 2.Charactersitics of Typical Municipal Effluent Treated Water

Reference	This Work			2
Location	OCWD, CA	DDSD, CA	Naperville, IL	Bay Area, CA
Total Dissolved Solids, mg/L	940	1190	555	869
Conductivity, mS/cm	2.2	1.8	0.9	
Total Organic Carbons, mg/L	10			
BOD 5-day, mg/L	19		3	8
pH	7.8	8.0	7.9	7.0
Sodium, mg/L as Na	230	248.3	88.0	76
Potassium, mg/L as K	19	16	12	5
Calcium, mg/L as Ca	82.0	52.1	64.0	76
Magnesium, mg/L as Mg	23.0	26.7	28.0	43
Barium, mg/L as Ba	< 0.1	< 0.1	< 0.1	
Strontium, mg/L as Sr	0.62	0.36	0.2	
Iron, mg/L as Fe	0.55	0.19	0.08	
Aluminum, mg/L as Al		0.4		
Chloride, mg/L as Cl		290.5	120	102
Sulfate, mg/L as SO_4		220.8	60	68
Bicarbonate, mg/L as HCO_3		305	171	396
Phosphate, mg/L as PO_4	2.5	0.6	2.0	6.0
Silica, mg/L as SiO_2	26.0	23.0	8.3	17.0

OCWD: Orange County Water District
DDSD: Delta Diablo Sanitation District

Assessment of impaired water characteristics to date confirmed that calcite is the most common potential cycle-limiting mineral and silica/silicate is also a common issue for impaired waters in the western region. For produced waters, barium sulfate and calcium sulfate are two additional potential cycle-limiting minerals. For reclaimed municipal wastewater effluents, calcium phosphate scaling can be an issue, especially in the co-presence of high silica. Computations of some of these industrial waters provided limitations of using impaired waters with current scale control technologies. Based on this analysis and discussion, we identified the need to develop calcium carbonate and silica/silicate inhibitors under high stress conditions.

Task 2. Develop High Stress Calcite and Silica Scale Control Chemistries:

As mentioned previously two methodologies were used in the development of scale inhibitors, namely, the static bench method and the Pilot Cooling Tower (PCT) simulation. Most of the work on initial screening of inhibitors was done using the static bench method and final evaluation was conducted using the PCT.

Silica Inhibitor:

Bench beaker tests were carried out to screen the efficacy of several inhibitors for silica control. The tests were conducted using a test solution with an initial silica concentration of 290-300 mg/L as SiO_2 at pH 7 and room temperature. During the course of the experiment, samples of the supernatant test solution were taken and the amount of soluble monomeric silica determined. A slower decrease of silica concentration indicates a more effective silica inhibitor. Three different inhibitor chemistries were tested at the dosage range of 20-100 mg/L:

- Silica Inhibitor A (S-A): A commonly used silica inhibitor, used as the benchmark in evaluations
- Silica Inhibitor B (S-B): A proprietary new chemistry
- Silica Inhibitor C (S-C): An alternative to S-A currently used at very limited sites for silica control

Results of the bench beaker tests are shown in Figure 2. Inhibitor S-B was found to be more effective than Inhibitor S-A at the same dosages.

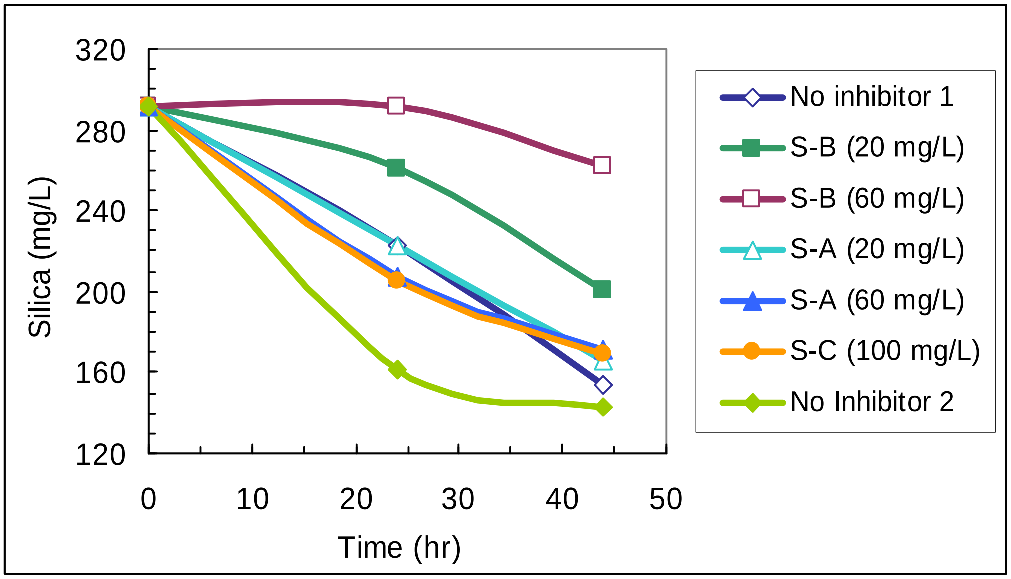


Figure 2. Results of bench beaker-tests for the evaluation of the silica inhibitors.

As shown in Figure 2, the molecule represented as S-B performed slightly better than the other two compositions, namely S-A and S-C. However, after about 20 hours, silica precipitation was obvious from the decrease in monomeric silica concentration. S-B composition showed improvement in performance at as the inhibitor concentration was increased, while S-A showed an opposite effect. Composition S-C showed the least efficacy for controlling silica precipitation.

Since the composition S-B showed the best performance we decided to prepare a larger batch of the sample (TX-138813) and further evaluate in a dynamic system using the pilot cooling tower (PCT). New silica inhibitor molecule S-B (TX 138813) continue perform better than the existing commercially available material S-A. We monitored both soluble and total silica. Soluble silica is the reactive silica that indicates the effect of inhibitor on silica polymerization and the total silica include the reactive silica and the polymerized silica, which is being dispersed. Although we are trying to inhibit silica polymerization to keep the silica in solution, but dispersion can also be helpful in preventing the fouling and help maximize the use of impaired water with high silica.

Figure 3. Pilot Cooling Tower (PCT)

The PCT shown in Figure 3 is used to simulate actual cooling tower conditions in terms of water flow velocity, heat flux, metallurgy, blowdown, and high efficiency fill. In this study we used the synthetic water to mimic impairment conditions. These cooling towers are equipped with Deposit Accumulation Testing Systems (DATS) units and Nalco's 3DT monitoring and control technology. 3DT technology allows controlling the product feed based on multiple fluorcent signals in addition to measuring conductivity, pH, ORP, and on line corrosion.

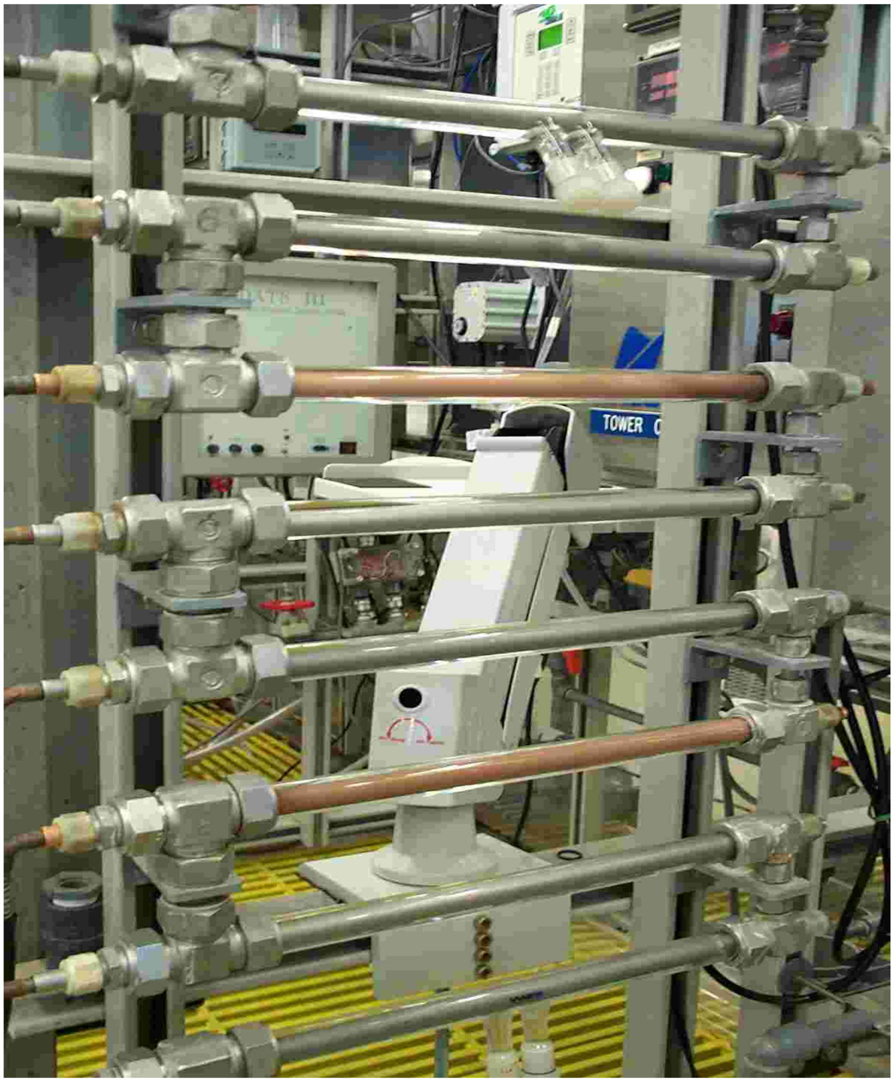


Figure 4. Pilot Cooling Tower –Heat Exchangers close up

As shown in Figure 4, the heat exchangers are made of different metallurgies to mimic field system. These heat exchangers are heated with electric heating cartridge of different wattage and by controlling flow and wattage; it is possible to simulate heat flux and outlet water temperature. The scale forming impaired water is on the shell side and the glass Plexiglas tubing allows visual inspection for any fouling of the heat exchangers

Initial studies using just sodium silicate were very encouraging, however when other ions common in natural water were added to the test water, the deposition was quite apparent at> 200 PPM silica as SiO_2. Although the heat exchangers did not show very much deposit but high efficiency fill and the plastic sump tank showed deposit. We were also losing both hardness and silica.

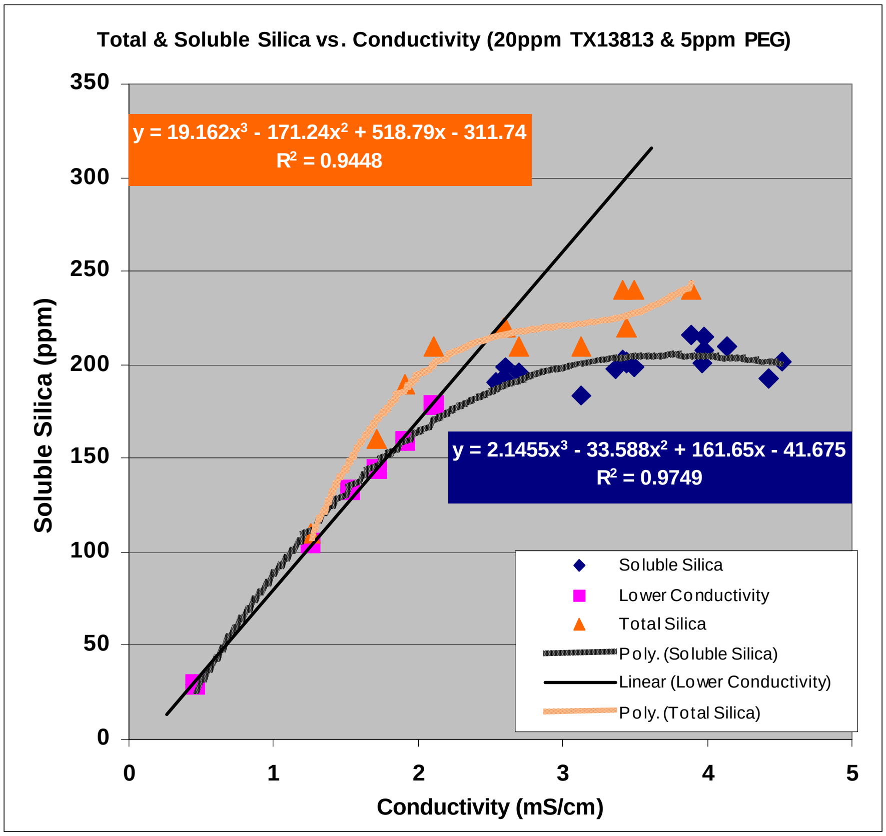


Figure 5. Results of PCT study with TX138813

In this graph (Figure 5), silica (both soluble and total) concentration is plotted against the conductivity in the recirculating water. The conductivity is a direct measure of the cycles of concentration in the PCT and also determines the theoretical level of ions in the water. The solid straight line is close to representing theoretical silica. At about the soluble silica concentration of 160 PPM, it seems to deviate from the cycles of concentration. However, it appears that we can still account for all the silica based on the total silica up to 220 PPM. As long as it is possible to account for the total silica in the recirculating water, silica deposition is not a problem. Once the theoretical silica exceeds 220 PPM, since we cannot find total silica in the water, it means it is being deposited in the system. So we are still falling short of our goal of >250 PPM total silica.

We ran several PCT runs to help determine the window of performance of the selected silica inhibitor using chemicals only. Such information is very useful to optimize the water treatment program using a combination of both EDI and the chemical treatment. The summary is provided in Table 3.

Table 3. Summary of the various PCT runs

PCT Tower	Program varied Dosage	Limiting Soluble SiO2 PPM	Limiting Total SiO2 PPM	Max Total SiO2 PPM	Notes
D	60 PPM SiO2 inhibitor + 100 PPM Scale/corrosion	190-200	200-220	240-260	Excellent MS and ADM corrosion
C	30 PPM SiO2 inhibitor + 100 PPM Scale/corrosion	180-190	190-205	220-240	Very good MS and ADM corrosion;
C	10 PPM SiO2 inhibitor + 100 PPM Scale/corrosion	170-185	180-200	210-240	Excellent corrosion Results
D	20 PPM SiO2 inhibitor + 5 PPM PEG+ 100 PPM Scale/corrosion	180-190	190-210	230-260	Excellent corrosion results

Based on this data it is evident that maximum level of silica that we can have in the cooling tower is ~250 PPM. Although we did not meet our original goal of 300PPM SiO2 but this data provided a good trend to help the synthesis of several additional samples. Results of silica control with one of these additional samples at different doses are tabulated in the following Table 4. We analyzed the test samples at different times to determine the effect of time on silica polymerization.

Table 4. Silica testing with laboratory prepared inhibitor sample

Testing Time	Blk	6107-79-5ppm	6107-79-10ppm	6107-79-20ppm
Initial	302.61	297.07	317.99	301.55
~1.5hrs	313.88	310.71	306.45	307.17
~2.5hrs	298.05	282.64	308.79	317.50
~3.5hrs	280.79	295.11	308.55	309.07
~4.5hrs	284.92	291.82	311.38	324.29
24hrs	156.68	234.80	291.59	300.24

The data show a significant improvement from 5PPM to 10 PPM and no significant gain at 20 PPM. The data is very encouraging. The performance of the new material synthesized in the laboratory met the goal of 300 PPM as SiO2. It seems (Figure 6) to inhibit silica polymerization up to 300 PPM soluble silica, which gives the hope that silica cycles can be doubled without causing fouling.

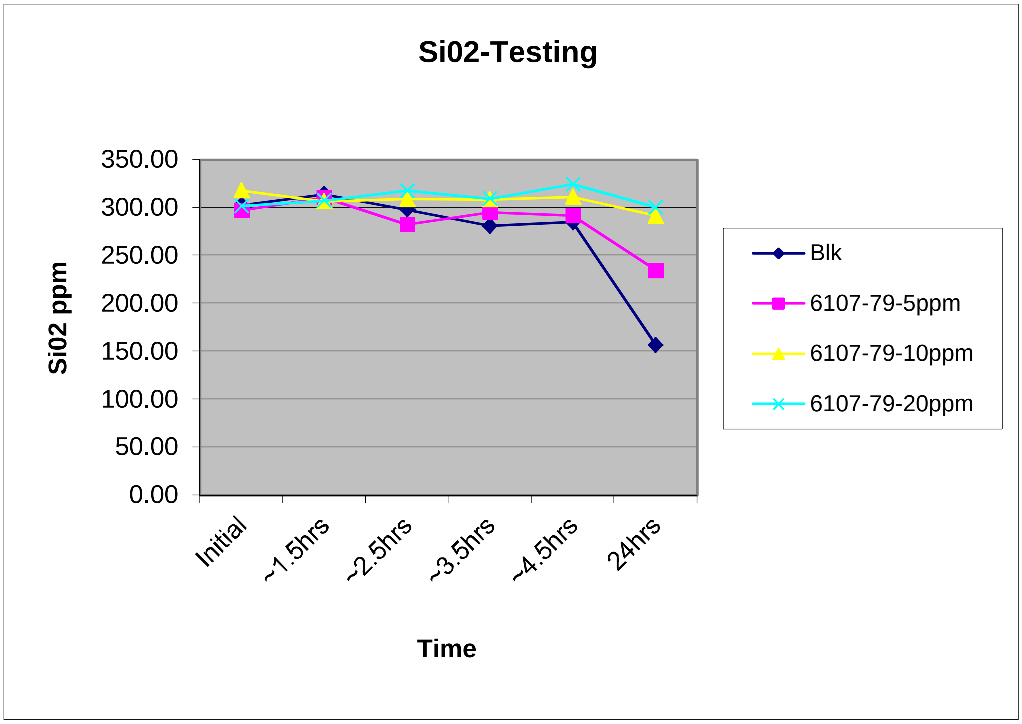


Figure 6. Effect of concentration of inhibitor on silica inhibition

We prepared several batches of this material to confirm the reproducibility of the silica scale inhibitor. The performance results are shown in Figure 7.

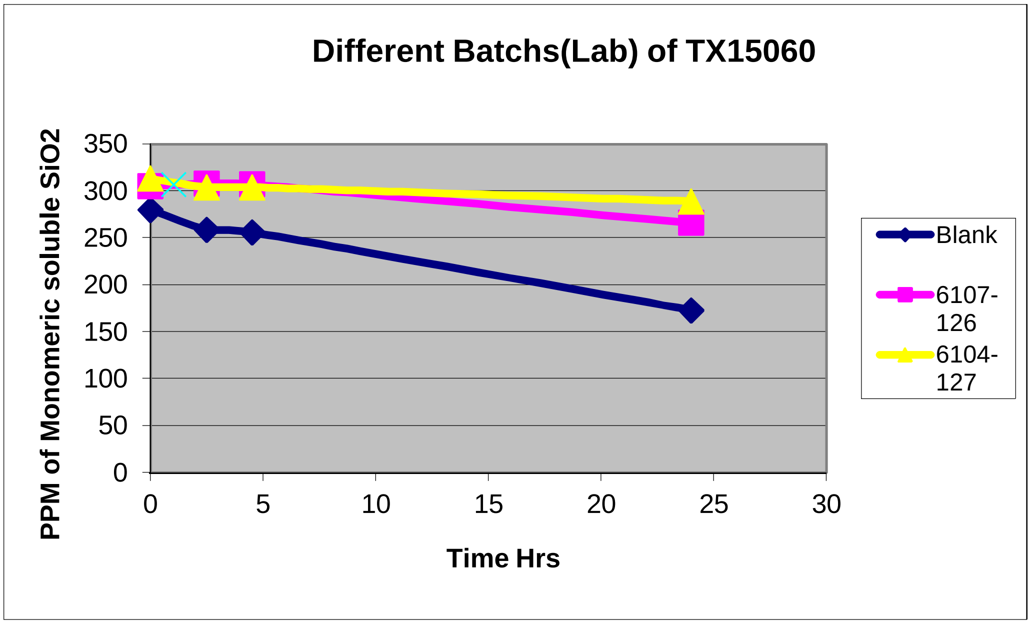


Figure 7. Performance of different batches of silica inhibitor

Silica Field Trial:

TX15060 name was given to the sample 6107-79 for further field evaluation and full scale production of the material. The new silica inhibitor was evaluated in the field at a western coal fired power plant. These waters have 20-40 PPM silica as SiO_2 and the water reuse is limited by silica. We have been able to increase the cycles of concentration from an average of 5 to 7-8 cycles without causing adverse effect on heat exchanger or condensers. We have been able to reduce the blow down from 276 gallons/minute to 158 gallons/min, a reduction of ~43%. Cold temperature did not affect the performance of the inhibitor, either; generally silica scale becomes more problematic in colder temperature.

Recent inspection of the heat exchangers confirmed the absence of any fouling (Figure 8 below). This is a heat exchanger bundle, the tubes are clean and there is only a very light dusting of powdery material on the tube sheet. This will neither hamper the heat transfer coefficient nor the flow of the water.

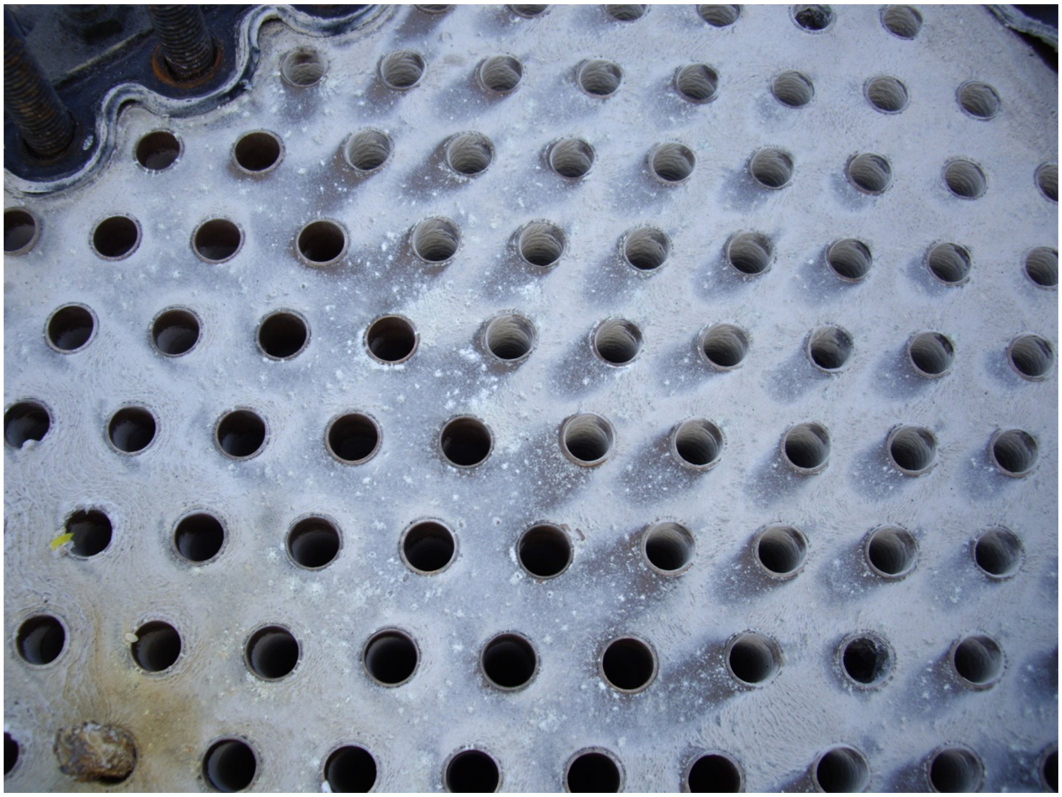


Figure 8. Heat Exchangers from the silica Field trial

One of the heat exchanger tubes was cut for inspection (Figure 9) and it was practically free of any deposit.

Figure 9. Heat Exchanger tube cut open for inspection

We also examined the high efficiency fill and Figure 10 shows that the high efficiency fill seems to be very clean; the deposit is seen only at the metallic structure holding the fill. This deposit is attributed to drying out of the salts in the recirculating water.

Figure 10. High efficiency PVC cooling tower fill from the field trial

Calcium Carbonate and calcium sulfate Scale inhibitor:

For an initial quick screening of different molecules at various concentrations a stagnant flask test was developed. The simple impaired is prepared using calcium chloride and a mixture of sodium carbonate and sodium bicarbonate. An 80/20 mixture of sodium bicarbonate/sodium carbonate in addition to providing the required alkalinity provides a buffer at pH 9.0. These flasks are dosed with different amounts of different inhibitor and are incubated for 24 hours in a water bath at 55 ^{o}C. At the end of the incubation time, each test solution is filtered through 0.22 • m membrane filter, while the solution is still hot. The filtrate is analyzed for calcium concentration using Atomic absorption spectrophotometer and complexometric titration to determine the %age inhibition using the following equation.

$$\% \text{ Inhibition} = \frac{V_E - V_o}{V_T - V_o} \times 100$$

Where: V_E = Total Calcium as mg/L for treated test sample
V_o = Total calcium as mg/L for untreated (blank) test sample
V_T = Total calcium as mg/L for calcium reference (initial) sample

The flask, which contains no inhibitor gives V_o, is considered at no inhibition (0%) and if V_E (treated with inhibitor) is equal to V_T, it will give complete inhibition (100%). V_T is determined from a flask, which contains only calcium and no alkalinity (or theoretical initial amount of calcium added to each flask.

Initially to create conditions of calcite saturation of 250X, the following composition of the water was synthesized:

150 mg/L Ca^{++}, 600 mg/L Alkalinity as $CaCO_3$ (80/20 $NaHCO_3/Na_2CO_3$), 266 mg/L Chloride, and 276 mg/L sodium.

The inhibitor solution is prepared as 0.5 g/L active concentration and its pH is adjusted to 9.0. The scale forming cations (calcium) and scale forming anions (the carbonate alkalinity) are separately heated in the water bath before these are mixed together. The inhibitor solution is added to the alkalinity solution. After mixing of the scale forming cations and anions, the solutions are incubated at 60^{o}C for 24 hours.

Results of the first series of tests are given in Table 5

Table 5. Results of calcium carbonate inhibition with different inhibitors

Inhibitor	Concentration mg/L	% Calcite Inhibition
L99BO	10	45.6
L99BO	20	100
L99BO	50	100
5636-130	20	44
5636-130	50	65
5636-130	100	62
5636-130	130	77
5636-130B	10	28
5636-130B	25	42
5636-130B	130	60

L99BO is a known phosphonate, which is effective in the test conditions; however this inhibitor can undergo degradation to orthophosphate under highly oxidative environment. In the cooling towers, oxidizing biocides are often used to control microbes in the water and to prevent biofouling. New compounds, 5636-130 and 5636-130B, were synthesized and evaluated. These new compounds are deemed more stable in an oxidizing environment than LLB90.

The two new inhibitors, 5636-130 or 5636-130B were not very effective compared to the existing material L99BO. Although L99BO is very effective scale inhibitor, however, L99BO is not very halogen resistant. Various types of oxidizing biocides are used to prevent biofouling in the cooling water. This is especially important in the use of the impaired waters that may contain tertiary sewage treated water. Although 5636-130 and 56130 B were not as effective as LL99BO for scale control, it was decided to evaluate these materials for scale control in the presence of bleach. Thus the standard flask test was modified where bleach was added to maintain 1.0PPM free chlorine. The results are tabulated in Table 6

Table 6. Effect of bleach on the effectiveness of scale inhibitors for calcium carbonate inhibition

Inhibitor	Concn. Mg/L	% Calcium Carbonate Inhibition	
		NO halogen	1.0FRH (bleach)
L99BO	10	45.6	38
L99BO	20	100	80
L99BO	50	100	95
5636-130	20	44	45
5636-130	50	65	60
5636-130	100	62	63
5636-130	130	77	75
5636-130B	10	28	30
5636-130B	25	42	40
5636-130B	130	60	60

We decided to combine these molecules with other known inhibitors for synergistic performance improvements. This was based on earlier studies with L99BO (US patent 5,772,923 and 5, 709814) that resulted in improving its performance and lowered the concentration needed for 100% inhibition. Another known good calcium carbonate inhibitor R-2531 was chosen to pair with 5636-130. The results are shown in the following graph (Figure 11) for a total concentration of 20 PPM.

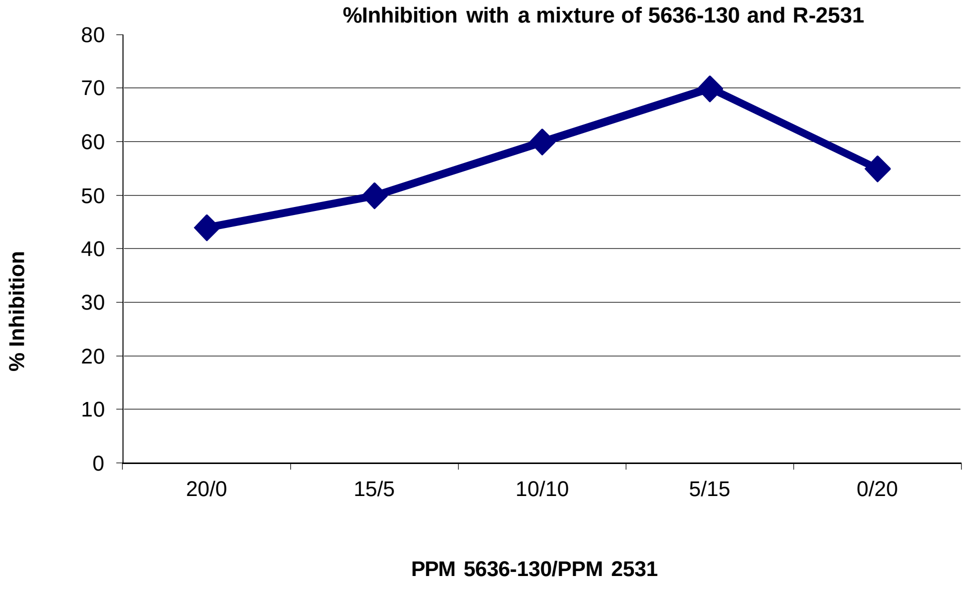


Figure 11. Calcium carbonate inhibition with combination of inhibitors.

Although these two inhibitors seem to show some synergism at 5PPM 5636-130 and 15 PPM R-2531, but it still did not match the performance of L99BO. A number of other similar experiments were done to find synergism with several of poly carboxyl and phosphino oligomers. The studies were also done at various concentrations of these combinations. Neither any combination nor higher dose resulted in performance equivalent or better than L99BO. Most other scale inhibitors have a very low tolerance for calcium, especially compared to L99BO, and many impaired waters will have high hardness.

The new material was synthesized and evaluated using standard 240X calcite test as described earlier. The compound 5786-56 was synthesized based on the discovery results of its precursor compounds 5636-130 and 5636-130B. The performance data is tabulated in Table 7

Table 7. 240X calcite saturation performance data

Flask	**Inhibitor**	**Vo**	**Ve**	**Vt**	**% Inhibition**	**ppm**
A	5786-56	150	300	400	60.00	15
B	5786-56	150	300	400	60.00	15
D	5786-56	150	300	400	60.00	20
E	5786-56	150	300	400	60.00	20
A	5786-56	100	350	400	83.33	50
B	5786-56	100	350	400	83.33	50
A	Formulation A	100	350	400	83.33	30
B	Formulation A	100	350	400	83.33	30
C	Formulation A	100	350	400	83.33	50
D	Formulation A	100	350	400	83.33	50
A	Formulation B	100	350	400	83.33	30
B	Formulation B	100	350	400	83.33	30
A	Formulation B	100	300	400	66.67	50
B	Formulation B	100	300	400	66.67	50

Vo is total calcium at equilibrium with no inhibitor
Ve is total calcium at equilibrium in the presence of inhibitor
Vt is the initial total calcium for the test

Based on this data, the performance of 5786-56 for inhibiting calcium carbonate is still lower than LL99B0. Two additional formulations A & B were created using compound 5786-56 and a non-phosphate low molecular weight water-soluble polymer. It appears the formulation A performed well. The lower performance for formulation B at higher concentration is perhaps due to its non-compatibility with calcium in the water. This phenomenon is quite common with many of the scale inhibitors used commercially, except for LL99B0.

At the end of this study, it appears that LL99B0 is still the most effective compound for inhibiting calcium carbonate.

Calcium sulfate:

In cooling tower, which has a very high alkalinity, sometime it is necessary to adjust the pH to maximize the cycles of concentration. In such cases the inhibitors are used to inhibit calcium sulfate scale. A bench test procedures was developed similar to the calcium carbonate bench test method. In this case test solution was prepared which contained 2500PPM as calcium ions, 4800 PPM as sulfate ions and 100 PPM as bicarbonate alkalinity. The test solution pH was adjusted to 7.5 and incubated fat 60C for 24 hours. At the end of the incubation period, the test solutions were filtered and analyzed for soluble calcium. The % inhibition was calculated using the same formula as described earlier for calcium carbonate. For the initial study L99BO was formulated with a dispersant AA/AMPS copolymer. The results are shown in the following graph (Figure 12).

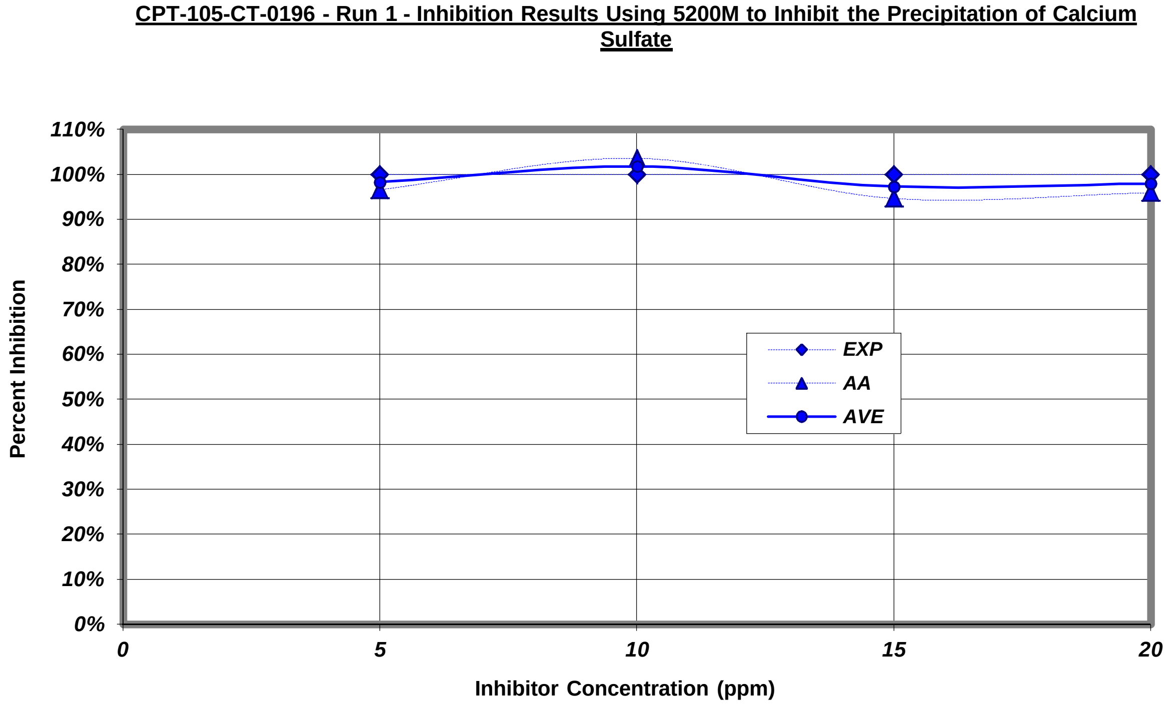


Figure 12. Calcium sulfate inhibition with 5200 M (Phosphonate/Polymer combination)

Although, initially we did not plan to do any calcium sulfate study with newly synthesized molecule), but based on the calcium carbonate inhibition data and halogen stability, it was decided to evaluate the performance of the new compound for calcium sulfate inhibition. Calcium sulfate inhibition study was done with 5786-56 using the standard test as described previously. The data is tabulated in table 8.

Table 8. Calcium sulfate Inhibition data

Flask	Inhibitor	Vo (ml)	Ve (ml)	Vt (ml)	% Inhibition	Inhibitor (ppm)
1a	5786-56	2000	2250	4750	9.09	2
1b	5786-56	2000	2250	4750	9.09	2
2a	5786-56	2000	3000	4750	36.36	5
2b	5786-56	2000	3250	4750	45.45	5
1a	5786-56	2500	3250	4750	33.33	5
1b	5786-56	2500	2750	4750	11.11	5
2a	5786-56	2500	4500	4750	88.89	10
2b	5786-56	2500	4500	4750	88.89	10

The data indicate that this new compound is effective for calcium sulfate inhibition, but uses fairly high concentration compared to LL99B0.

Thus at this point, the best inhibitor for both calcium carbonate and calcium sulfate is some combination that contains L99BO. All efforts have been unsuccessful in finding a new inhibitor that could outperform LL99B0. We further focused on developing the window of performance of LL99B0 in the impaired waters defined during the beginning of this project. Bench scale experiments were carried out using a matrix of conditions and the limits are defined in terms of calcium hardness, alkalinity and pH using fresh water conditions. True precipitation inhibitions conditions are defined when there is no loss of soluble calcium after 48 hours of incubation at 140°F in a dynamic condition. These conditions lead to a calcite saturation of 220-240X the equilibrium solubility corrected for ionic strength and temperature. The performance window was also tested against synthetic “Gillette, WY CBM type water, the chemistry of this water is defined in Table 1. The conditions were simulated to mimic 10 cycles of concentration. The study showed that in order to use this water, using chemical inhibitor only, either the cycles of concentration has to be lowered from 10 to 1.5, or pH should be adjusted to 10.0 using a large quantity of acid in order to increase the reuse of this water to 10 cycles.

Ion Removal Technology under CRADA:

The third alternate is to remove bicarbonate using ED or EDI as shown by ANL work described below. The optimization step (cost and maximum reuse of water) is to blend the two technologies. In the next section of the report developmental and work is reported, where some of the ions are partially removed from the impaired water and recycled to determine the scaling tendencies and maximize the impaired water reuse at the lowest cost

One of the membrane systems being tested by Argonne for the removal of scaling components is resin wafer electrodeionization (RW-EDI). EDI is an industrial process that incorporates ion-exchange (IX) resin beads into an electrodialysis (ED) stack. ED is an electrically-driven membrane-based separations process. Commercial EDI systems are constructed by filling the diluate channel in an ED stack with loose ion exchange resin beads. Argonne has immobilized the loose IX resin beads with polyethylene resins to form a porous resin wafer (RW) material. A typical EDI system schematic is shown in Figure 13.

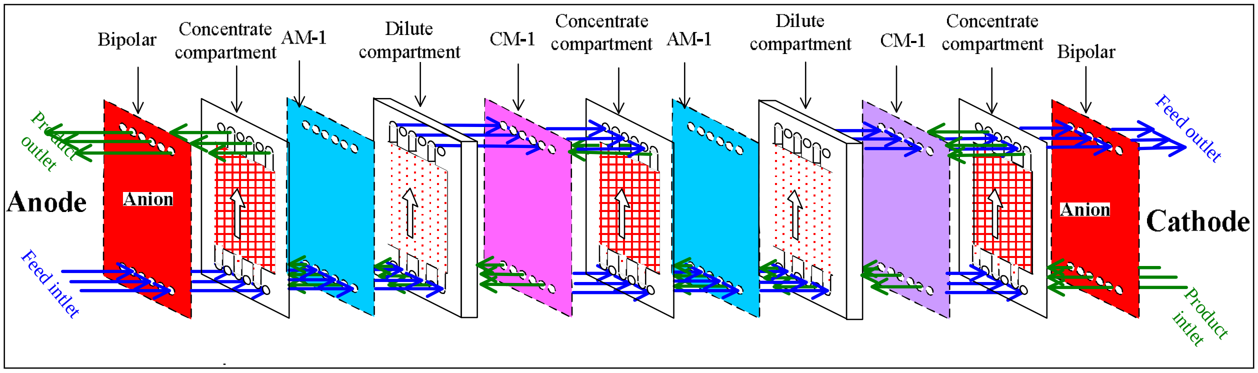


Figure 13: Schematic of the EDI system used for scaling ions removal

The RW-EDI platform enables in-situ pH control by using the water splitting reaction which eliminates or minimizes the need for acid or base additives. The RW-EDI platform provides flexibility in terms of membranes used and their configuration. Additionally, the wafer resin composition can be varied (anion excess, cation excess or equal amounts of anions and cations) to facilitate the removal of scaling components.

Materials and Experimental Setup

Electrodialysis (ED) System

Argonne used two different ED systems during the testing. While investigating hardness removal in simulated make-up water, a four-cell pair stack comprised of Ameridia's CMX-s and AHA-1 ion exchange membranes was used. Hardness removal from simulated 10-cycled power plant cooling water was done with a 6-cell pair ED stack using Ameridia's AM-1 and CM-1 ion exchange membranes.

Electrodeionization (EDI) System

The Argonne EDI resin wafers were fabricated from commercial grade gel-type strong acid cation and strong base anion exchange resins. The resin wafers with different ratios of cation/anion exchange resins were fabricated using Argonne's patented process (Patents 6797140, 7306934, and 7452920). Commercial polymeric ion-exchange membranes were used to assemble the RW-EDI stack. Different membrane configurations were tested during process development. A commercial ED stack was used as the base template to assemble the EDI stack. Two different EDI stack sizes were employed which had a total membrane area of either 14 cm^2 or 195 cm^2. Argonne's in-house gasket material was used to seal the resin wafers in the stack.

The feasibility of using ED to reduce the hardness and hence the scaling potential of power plant recirculated cooling water and make up water was tested by Argonne at the bench-scale. Ten liters of simulated make up water, which contained 995 mg/L of NaCl equivalent, was tested in a four-cell pair ED stack which used Ameridia's CMX-s and AHA-1 ion exchange membranes.

The results showed a 99+% removal of salts from the simulated solution with low power consumption. Simulated 10 cycled cooling water containing 8500 mg/L of NaCl equivalent and 1.3 meq hardness was tested in a six-cell pair ED stack built with Ameridia's AM-1 and CM-1 ion exchange membranes. This test showed a 99+% removal of salts from the simulated solution with very low power consumption. The divalent cations were removed preferentially over the monovalent cations. These results suggest that it is technically and economically feasible to use ED for the separation of scaling species from reused water.

Argonne also tested the feasibility of using EDI to reduce alkalinity in simulated recirculated cooling water and make up water. Reducing alkalinity could potentially increase the number of times the cooling water could be recirculated. Bench-scale EDI stacks were assembled using Ameridia's CMX-s and AHA-1 ion exchange membranes and porous wafers which were molded from a mixture of ion exchange resins. Initial screening runs were done with a four –cell pair mini-stack (14 cm^2 membrane area/cell pair) while subsequent runs were done with a larger six cell-pair stack (195 cm^2 membrane area/cell pair). Two different simulated waters were used – one with 2500 ppm of NaCl equivalent and 2700 ppm of alkalinity and the other with 3500 ppm of NaCl equivalent and a similar 2700 ppm of alkalinity. For these tests, the power required to remove high levels of alkalinity from the simulated water was around 2 – 3 kWh/100 gal of water. Although the EDI system could remove the alkalinity, it was not preferentially removed compared to the other salts because the pH of the processed effluent was not low enough.

The EDI system's selectivity was improved by changing the ratio of cation and anion ion-exchange resin beads in the wafers. Three different wafers were tested: an anion-excess resin wafer, a cation-excess resin wafer and a wafer made with equal amounts of cation and anion resins. Of these three, it was found that the wafer made with an excess of cation resin gave the best separation efficiency.

An EDI stack with these optimized resin wafers was then tested. Two different simulated waters were used – one with 9600 ppm of NaCl equivalent and 4600 ppm of alkalinity and the other with 3500 ppm of NaCl equivalent and 6400 ppm of alkalinity. The results showed low power consumption and over 98% removal of the alkalinity from the simulated waters.

In addition to the removal of hardness and alkalinity, the removal of silica was also studied with bench-scale ED and EDI. These technologies were tested using a simulated impaired water solution which contained 200 ppm of silica. Both ED and EDI demonstrated the ability to remove silica from the simulated water. The power consumption for EDI was approximately 25 – 30% less than the power consumption observed for ED.

In this task, Argonne focused on two different objectives – assessment of the integrated process design and the optimization of EDI alkalinity removal from reused water.

The first objective was to assess the process design that integrated the ED or EDI system with a chemical treatment system that maintained the water quality while improving the number of water reuse cycles. As part of this work, Argonne developed a process model to help determine the benefits and drawbacks of the different integration configurations. The parameters considered included the desalting efficiencies at different alkalinity concentration levels (5000 ppm or 500 ppm), electrical cost, processing flux and the preliminary capital cost of the ED or EDI module. The assessment served as a guide for the overall system integration efforts. It also helped to set technical goals for the pilot-scale demonstration and evaluation using the integrated system.

The second objective addressed the need for further optimization of alkalinity removal with EDI. In order to improve the alkalinity removal efficiency, resin wafers with different ratios of cation and anion resin beads were evaluated in an EDI system. Table 9 provides a comparison of the observed processing flux and power consumption when the alkalinity was reduced from 2400 ppm to 1000 ppm. The data suggests that the excess cation resin wafer has the best performance (high processing flux and low power consumption) during alkalinity removal.

Table 9. Comparison of Alkalinity removal using EDI with different resin wafers

Resin Wafer Composition	Processing Flux (gal/m^2/hr)	Power consumption (kWh/100 gal)
Excess Cation	11.5	2.8
Excess Anion	2.0	19.8
Excess Cation (weak acid)	2.8	38.0

Based on this data, Argonne assembled an EDI stack with the optimal resin wafer composition. A series of tests were done to determine the effect of stack configuration and the type of ion exchange membranes on the EDI system's alkalinity removal efficiency. Table 10 shows the optimized performance while Table 11 shows the estimated capital cost based on the process performance in Table 10.

Table 10. Optimized Process Performance

Process Salt content		Processing Flux (gal/m^2/hr)	Power consumption (kWh/100 gal)
Initial (ppm)	Final (ppm)		
5000	500	5.9	3.7
500	50	19.5	0.68

Table 11. Estimated Processing Cost Based on Performance Shown in Table 10

Impaired Water Flow Rate (gal/day) (gal/hr)	100,000 4,167	100,000 4,167
Alkalinity Concentration (ppm)	5000 to 500	500 to 50
Processing Flux (gal/hr/m^2)	5.9	19.5
Power Consumption (kWh/100 gal)	3.73	0.68
Capital Cost Range	\$1,056,250 - \$1,408,333	\$320,724 - \$427,632
Power Cost \$/day at 5 cents/kWh \$/year	\$187 \$68,103	\$34 \$12,495

The optimized EDI system was able to increase the processing flux fourfold. It also reduced the power consumption by 20% compared to what had been previously reported. The fourfold increase in processing flux provides significant savings (75%) in the capital equipment cost.

In order to reduce membrane fouling and lengthen the time between CIPs, Argonne further optimized the EDI desalination process by modifying membrane configuration and operating conditions. An anti-fouling chemical developed by Nalco (pHREEdom 5200 M) was also tested but the precipitation that was causing the membrane fouling did not decrease. In the enhanced process, the removal efficiencies of hardness, alkalinity and total salt removal were improved, as shown in Table 12. The cost of water desalination using EDI was estimated to be approximately $0.05/barrel of water, as shown in Table 13.

Table 12. Performance of the Enhanced EDI System with Fouling Reduction

Process Salt content		Processing Flux ($gal/m^2/hr$)	Power consumption (kWh/1000 gal)	Salt Removal	Hardness Removal	Alkalinity Removal
Initial (ppm)	Final (ppm)					
500	50	19.5	0.57	87.0%	83.2%	86.0%
500	50	19.2	0.54	95.1%	88.8%	99.5%

Table 13. Estimated Processing Cost Using the Enhanced EDI System

Impaired Water Flow Rate (gal/day) (gal/hr)	100,000 4,167
	Make up water
Salt Concentration: Influent à Effluent (ppm)	500 • 50
Processing Flux ($gal/hr/m^2$)	19.2
Power Consumption (kWh/100 gal)	0.5366
Effluent pH	5.7
Capital Cost Range	$325,000 – 433,333
Electrical Cost $/day at 5 cents/kWh $/year KW	$27 $9793 22

Pilot study with PCT (EDI and Scale Inhibitor):

In the final phase of the project the ANL-Nalco team evaluated the pilot-scale use of EDI desalination for the synthetic make-up water found in power plant heat-exchangers. Initial testing using PCT and EDI resulted in fouling of EDI membrane due to precipitation of calcium sulfate in the concentrate tank. To solve the membrane fouling issues on the concentrate compartment (i.e., waste water recirculation) the ANL team optimized further the EDI desalination process. In the optimized process, the removal efficiencies of hardness, alkalinity and total salt removal were enhanced. Table 14 shows the latest results. The economics of water desalination using

EDI was estimated to be around $0.07/barrel water; that figure includes both capital and operating costs. .

Table 14. Desalting Performance of Revised EDI System

Process Range Salt content	Experiment Date	Processing (gal/m^2/hr)	Power consumption (kWh/100	Salt Removal	Hardness Removal	Alkalinity Removal
500 to 50 ppm	Dec-08	19.5	0.57	87.0%	83.2%	86.0%
500 to 50 ppm	Mar-09	19.2	0.54	95.1%	88.8%	99.5%

A synthetic impaired water is brought into the EDI unit and the soften water (with impaired ions removed) is used as a makeup water to the Pilot Cooling Tower. CRADA partner, ANL, constructed the proto type EDI unit. The unit was properly sized to meet the makeup requirements for the PCT. After the shake down of the combined unit, several runs were planned to evaluate the efficacy of the concept in terms of maximizing the cycles, economics of >95% ion removal (power consumption), partial removal of impaired ions and combination with inhibitors, and Ion removal from the makeup water as well blowdown water.

We conducted this study by approaching from two different scenarios:

1. Removing the impaired ions using EDI upfront from the makeup water
2. Removing the impaired ions using EDI from the blowdown of the cooling tower

Both approaches provided excellent results indicating the possibility of operating cooling tower using water with impaired ions close to zero liquid discharge. In this system the small wastage of the water came from blowing down the concentrate (about 23 liters) twice per week and another small volume (about 20 liters per week) for cleaning in place (CIP) and the rinse. The results of these studies are tabulated in the following tables.

Table15. PCT study using makeup water as feed water to EDI

SAMPLE I.D.	EDI MU	ER	CONC.	DI Product	CONC.
SAMPLE DATE	11/5/2009	11/5/2009	11/5/2009	11/5/2009	11/5/2009
SAMPLE TIME	10:30	10:30	10:30	10:30	2:45
SAMPLE VOLUME	120ml	120ml	120ml	120ml	120ml
pH	8.43	1.51	1.99	6.57	1.94
CONDUCTIVITY	680	24300	20700	323	21000
M-ALK	118	0	0	24	0
CALCIUM UF	135	0.48	28.9	35.6	445.75
MAGNESIUM UF	73	0.16	9.44	18.8	8.63
CHLORIDE	124	824	159	81	8967
SULFATE	60	4500	22	0	215

SAMPLE I.D.	EDI MU	ER	CONC.	DI Product	EDI MU
SAMPLE DATE	11/6/2009	11/6/2009	11/6/2009	11/6/2009	11/9/2009
SAMPLE TIME	14:45	14:45	14:45	14:45	15:00
SAMPLE VOLUME	120 ml	120 ml	120 ml	120 ml	125
pH	8.3	1.49	1.95	6.75	8.29
CONDUCTIVITY	683	17400	22300	215	698
M-ALK	112	0	0	37	118
CALCIUM UF	142.75	7.63	153	37.32	145.8
MAGNESIUM UF	2.17	2.8	2.2	21	2.24
CHLORIDE	126	2776	10035	54	128
SULFATE	70	430	335	22	70

Table 16. PCT study using cooling tower blowdown as feed water to EDI

SAMPLE I.D.	Conc.	Prod.	CIP	Feed (PCT Basin)	Conc.
SAMPLE DATE	11/20/2009	11/20/2009	11/20/2009	12/21/2009	12/21/2009
SAMPLE TIME	13:55	13:55	13:55	16:30	16:30
SAMPLE VOLUME	120ml	120ml	120ml	120ml	120ml
pH	1.87	6.85	0.9	7.7	2.04
CONDUCTIVITY	26700	335	66400	1439	20800
M-ALK	0	52	0	88	0
CALCIUM UF	2304.4	63.5	438.5	339.5	208.5
MAGNESIUM UF	1286.5	33.25	159.5	145.25	101.5
CHLORIDE	10980	80	9059	318	8540
SULFATE	950	42	200	200	95
SAMPLE I.D.	Feed (PCT Basin)	Conc.	Prod.	Feed (PCT Basin)	ER
SAMPLE DATE	12/22/2009	12/22/2009	12/22/2009	12/23/2009	12/23/2009
SAMPLE TIME	15:32	15:32	15:32	9:05	9:05
SAMPLE VOLUME	120 ml	120 ml	120 ml	120 ml	120 ml
pH	8.01	1.63	4.54	8.06	1.23
CONDUCTIVITY	350	24400	92	256	30100
M-ALK	41.6	0	8.8	36	0
CALCIUM UF	68.25	701.75	13.5	45.92	30.27
MAGNESIUM UF	33.5	383.25	7.36	26.32	11.97
CHLORIDE	122	9638	79	79	1830
SULFATE	375	475	0	500	9000

As can be seen in Tables 15 and 16, the concentrate tank conductivity is increased from 350 • S/cm^2 to >30,000 • S/cm^2, although some of the conductivity in the concentration tank comes from sodium chloride added as a means of conducting solution. Initial problem of calcium sulfate precipitation of calcium sulfate was solved and in these experiments it showed no sign of fouling and decrease in flux.

We continued working on comparing the removal of impaired ions from the makeup water versus from the blowdown discharge in the matrix of water saving, energy consumption, and footprints. Several water samples with various degrees of impairment were used to remove 90-95% of all the ions in the water. The makeup water has 500-2000 PPM TDS (total dissolved solids) and the blowdown from the PCT consisted of 4000-9000 PPM TDS. The power requirements for the makeup water were 30% of the power requirements for the blowdown. Much larger volume has to be processed for the makeup water compared to the blow down to account for the constant volume of evaporation. The evaporation volume remains constant regardless of the cycles of concentration of the cooling tower. The volume of the blow down is significantly reduced with increase cycles of concentration, e.g., the blowdown decreased by

50% with doubling the cycles of concentration during our study. However, the estimates are that there is no difference in the water savings for either treating the makeup water or the blow down. Most of the water discarded is either CIP or the concentrate as reported in the last quarterly report. In a zero liquid discharge system, removal of TDS from the blowdown stream is more cost effective than removal of TDS from makeup water, due to processing of less volume through EDI, even though former requires higher power consumption than the latter.
A long-term integrated evaluation (550 hours) of Argonne's optimized EDI system was performed at Nalco's cooling tower water testing facility. Operation was done by Nalco personnel with technical oversight and guidance provided by Argonne personnel. Synthetic make-up water similar to a power plant's cooling tower make-up was used as the feed to the EDI stack. The EDI system produced 220 L/day of treated water with 90%+ salt removal. The treated water was suitable for use as make-up water at a power plant. Over 850 gallons of high purity "make-up" water was generated during the long-term testing period. During this time the electrical cost was 0.6 kWh/100 gal water.

The EDI system's desalination performance was stable when the salt concentration in the concentrate compartment (i.e. the EDI waste stream) was controlled. No fouling on the cation ion-exchange membranes was observed. A clean-in-place (CIP) was needed after every 48 hours of operation time to prevent accumulation of precipitation from hardness and bicarbonate ions at the inlet to the EDI resin wafers.

In the final analysis for any size cooling tower the water consumption is through evaporation, blowdown and some leaks. The evaporation rate depends on the recirculating rate and delta temperature; it remains constant at any cycles of concentration. Increasing cycles of concentration from 5 cycles to 10 cycles reduces blowdown by 55% and the blowdown rate is 25% of the evaporation rate, which means 75% water consumption is due to evaporation. By further increasing cycles of concentration from 10 to 15 cycles, there is further reduction of 15% in blowdown rate; however 93% water consumption is comes from evaporation. Thus there is a much more water savings from 5 cycles to 10 cycles than going from 10 cycles to 15 cycles of concentration. Beyond15 cycles of concentration, there is practically very little water savings. In real industrial cooling towers, many of the systems due to leaks have hard time even attaining 10 cycles of concentration. Cost and environmental regulations must also be considered to select the cycles of operation. The cost to remove impaired ions and chemically treat the water increases significantly as the salt concentration is increased. The discharge of water containing high salinity is also regulated. The most economical approach we found is to partially remove the scale forming ions from the blow down water (less volume) and maintain ionic concentration in the recirculating water that can be easily treated with the new scale inhibitor reported in this report.

As reported earlier in this report the total cost of water treatment with EDI is ~ $0.07/barrel of water, including both capital and operating costs. It is broken down to ~ 3.0c/barrel capitol & ~4.0c/barrel of operating cost. This assume electric rate of 5c/KWh. At a flow rate around 0.45 barrel/hour/m2 of capital cost at ~$350k. The foot prints are very small. The only chemical used in EDI is sodium chloride in the concentration chamber as electrolyte. In actual operation the chemical cost is reduced at least by 50-60-% by 50% removal of the scale forming ions using EDI. The combined cost of both silica and calcium carbonate inhibitor is ~$30-40/million pound of blowdown. Cost of the new silica inhibitor has been reduced at least by 67% compared to existing silica inhibitors. Additional chemical cost may incur due to addition of corrosion inhibitors and biocides.

Acknowledgements:

Financial support for this project was provided by Nalco Company and DOE. Dr. Seth W. Snyder, Dr. Yupo J. Lin and Mr. Michael Henry of Energy Systems Division, Argonne National Laboratory are thanked for delivering results under CRADA #C0600501. The author is also grateful for the contribution of various other team members from Nalco Company - Dr. S.P.Tsai, Dr. S. Kidamibi, Dr. Frank Lu , Ms. Cheryl Williams, Dr. N Greene, Dr. K. Fivizzani, Dr. A. Sommese, and Dr. J Schwartz.

Intellectual Property

No inventions were developed as part of this CRADA.

Enabling background intellectual property with potential for non-exclusive license:

1. U.S. Patent 6,495,014, R. Datta, Y. Lin, D. Burke; S.-T. Tsai, "Electrodeionization substrate, and device for electrodeionization treatment"
2. U.S. Patent 7,452,920, Y. J. Lin, M. P. Henry, S. W. Snyder, "Electronically and ionically conductive porous material and method for manufacture of resin wafers therefrom"
3. U.S. Patent 7,507,318, Y. J. Lin, M. P. Henry, S. W. Snyder, E. St. Martin. M. Arora, L. de la Garza, "Devices using resin wafers and applications thereof"

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2. DiFilippo, Michael. (2003), *Use of Degraded Water Sources as Cooling Water in Power Plants*, EPRI, Palo Alto, CA and California Energy Commission, Sacramento, CA: 2003. 1005359.
3. DiFilippo, Michael. (2004), *Use of Produced Water in Recirculating Cooling Systems at Power Generating Facilities, Deliverable Number 3: Treatment & Disposal Analysis*, Semi- Annual Technical Progress Report, U.S. Department of Energy Award No. 41906, October 20