

Innovative Ion Exchange Systems for Cost-Effective Increase in Water Re-Use in Power Plants

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ABSTRACT

The power generation industry is adopting water conservation and recycling measures to address concerns about water usage and rising overall costs of water. These measures can result in dissolved solids (TDS) that accumulate in process streams including cooling and utility water, ash pond water, and FGD wastewater. Rising levels of Ca, Mg, and SO_4 limit the extent of water re-use by affecting the scaling potential of process water, while dissolved Ca, Mg chlorides increase the boiling point of waste liquors treated in ZLD evaporator-crystallizer systems leading to increases in power consumption and capital cost of ZLD systems. BioteQ's innovative ion exchange processes provide a new cost-effective way of controlling Ca, Mg, and SO_4 in process water loops, increasing water re-use while decreasing overall water costs. Unlike membrane or conventional IX systems, these ion exchange processes do not produce brine waste, maximize water recovery, operate in the presence of suspended solids and/or on waters with high scaling potentials without any need for pre-treatment, and use low cost reagents such as lime for resin regeneration. The product streams include only treated water and solid by-products composed of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$. Case studies of the innovative IX system applied to ash pond water, cooling water, and ZLD system are presented and life cycle cost-benefits are discussed.

BACKGROUND

WATER USE BY POWER PLANTS

In certain areas of the world water has become a commodity and fossil fuel fired power plants located in these areas are faced with the challenge to conserve as much water as possible. Table 1 summarizes the consumption of water by coal fired power plants (EPA 2008; Merkle 2008). As can be seen from this table, cooling water accounts for the largest portion of the overall consumption, followed by ash handling, and FGD scrubber make-up water. The cooling water consumption is composed of a) evaporative losses which are a function of

the overall thermal efficiency of power plants, and b) cooling tower blow-down which is a function of the cooling water quality and can account for up to 35% of the total cooling water consumption. It is an unfortunate reality that fresh water that is available in regions of water scarcity is often of very poor quality, i.e.: with elevated TDS and hardness levels.

The data shown in Table 1 represent true water consumption as opposed to usage in that the water volumes listed in Table 1 either evaporate or become unusable due to the build-up of various constituents that prevent further reuse and/or discharge of this water into the environment. Table 2 and 3 summarize the most common limitations to water reuse and discharge into the environment, respectively.

Table 1: Water Use by Coal Fired Power Plants

Water Use	Consumption by Coal Fired Power Plants (GPM/MWe)	Factors Affecting Water Consumption
Cooling Tower	12 to 21	thermal efficiency of power plant; make-up water quality
Ash Handling	0.3 to 1.2	dry or wet flue and bottom ash handling
FGD Scrubber	0.2 to 0.7	Sulfur content of coal, gypsum slurry dewatering, design of FGD scrubber
Boiler Feed	0.01 to 0.06	Leakage in steam lines, quality of boiler feed water

Table 2: Limitations to Water Re-use

Water Constituent	Negative Effect Associated with Water Reuse	Source of Constituent
Ca	carbonate or gypsum scaling	make-up water, limestone used in FGD, ash in contact with water
SO ₄	gypsum scaling	H ₂ SO ₄ used for Alkalinity control, sulfur from coal
Cl	corrosion	make-up water, HCl used for softening
Si	scaling / silica species	make-up water
TDS	air emissions PM _x / drift from cooling towers	all of the above (Ca, SO ₄ , Cl, Si all contribute to TDS)

Table 3: Limitations to Water Discharge

Water Constituent	Reason for regulations	Source of Constituent
Hg, Se, other heavy metals	toxicity to aquatic life and humans	make-up water, limestone used in FGD, ash in contact with water
SO ₄	toxicity to livestock, irrigation and drinking water standard 250 mg/L	H ₂ SO ₄ used for Alkalinity control, sulphur from coal
TDS	impact on aquatic life and fresh water re-use downstream	make-up water, HCl used for softening

As can be seen from Tables 2 and 3, elevated levels of calcium hardness, sulfate, TDS, and Si are amongst the most common limitations for water re-use and/or discharge and the main source of these constituents is the fresh make-up water drawn from groundwater aquifers, lakes, or rivers. It follows that power plants that are most challenged in terms of the overall water management are those that rely on a source of water that contains elevated TDS and hardness such as for example the Colorado River water or water drawn from parts of the Ogallala aquifer. Power plant wastewaters that cannot be reused or discharged are directed to Zero Liquid Discharge (ZLD) systems consisting of solar ponds where water evaporates and/or salts crystallize or mechanical evaporator-crystallizer units where salt crystallizes at elevated temperature and water is recovered in the form of condensate.

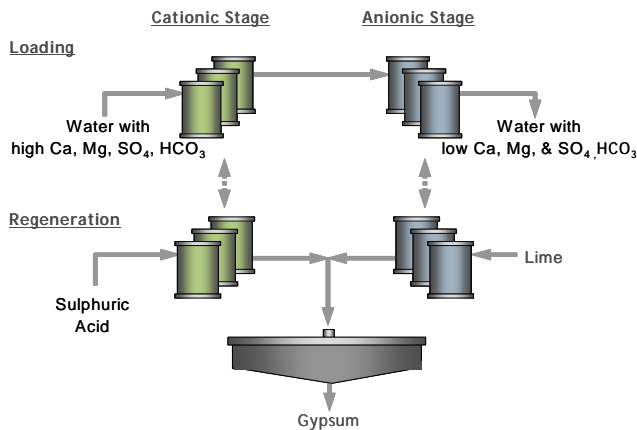
PROCESS DESCRIPTION

SULF-IX PROCESS

BioteQ has developed the Sulf-IX™ process specifically for the removal of TDS from hard waters with a high scaling potential and elevated level of sulfate. Sulf-IX is a two stage ion exchange process employing one cation and one anion resin placed in two separate circuits operating in series achieving an overall partial demineralization of the feed by selectively removing Ca²⁺, Mg²⁺ and SO₄²⁻ from the Sulf-IX plant feed water. The feed is first directed to the cation circuit operating with a Strongly Acidic Cation (SAC) resin where Ca and Mg are removed. The effluent from the cation circuit is then directed to the anion circuit operating with a Weakly Basic Anion (WBA) resin where H₂SO₄ produced in the cationic circuit is taken up by the resin. Ion exchange reactions during resin loading are identical to those utilized in conventional ion exchange systems. The unique feature of the Sulf-IX process is the regeneration step which is accomplished by using H₂SO₄, and lime, as the regenerants for the cation and anion resins, respectively. In both cases solid gypsum is formed during resin regeneration. The cationic gypsum is then blended with the anionic gypsum to yield a final neutral gypsum product.

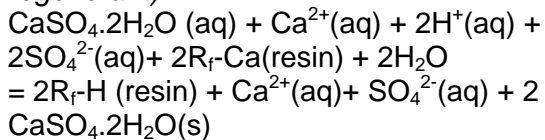
The schematic of the Sulf-IX process is shown in Figure 1.

Figure 1: Sulf-IX Process Schematic

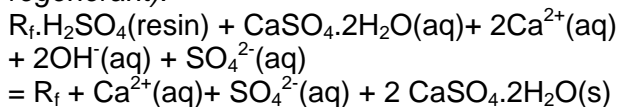


The unique feature of the Sulf-IX process is that the spent regenerants from the cation and anion circuits are quantitatively recycled with only a small volume of concentrated sulfuric acid and lime added to the recycle stream to make-up for the acid and hydroxide consumed by the IX process. The resin regeneration reactions taking place in the cation and anion stages can be described by reactions (1) and (2):

(1) *Cation Resin Regeneration (100% recycle of regenerant):*



(2) *Anion Resin Regeneration (100% recycle of regenerant):*



where (s), (aq), and (resin) stand for solid, solution, and resin/gel phases respectively, and R_f depicts the resin functional groups. The formula of undissociated gypsum species CaSO₄·2H₂O (aq) is included on both sides of the reactions (1) and (2) in order to highlight the fact that as a result of the regenerant recycle, the regeneration of resins in Sulf-IX takes place

under gypsum saturation conditions in the bulk of solution.

Magnesium is removed together with Ca in the cation stage of the Sulf-IX process. However, since magnesium sulfate is more soluble than calcium sulfate, Mg ions, unlike calcium ions, accumulate in the regenerant. In order to maintain a constant magnesium removal by the IX resin in the cation circuit, a portion of the cationic regenerant is bled into a small Mg removal circuit where Mg is removed from solution as either CaMg(CO₃)₂ or Mg(OH)₂ by reacting with CO₂ or lime.

Figure 2A: 25 m³/hr Sulf-IX column



Figure 2B: 200 L/hr Sulf-IX Column



Figures 2A and 2B show the small demonstration pilot unit of Sulf-IX operating at 200 L/hr (55 GPH) of continuous feed, and a large unit operating at 25 m³/hr (110 GPM).

If there is bicarbonate alkalinity present in the feed water, CO₂ degassing is carried out downstream of the cation stage prior to the discharge from the cation stage entering the anion stage.

The key advantages of Sulf-IX can be summarized as follows:

- Process operates on hard scaling water and in the presence of suspended solids without any pre-treatment as the process operates with fluidized bed of resins;
- Solids, i.e. gypsum, dolomite, or Mg(OH)₂ are the only waste by-products of the process. No brines are produced;
- Process achieves very high water recovery since the only water lost in the process is the pore water contained in the solids products;
- Process has lower operating costs than membrane systems or conventional IX systems due to inexpensive regenerants, and low power consumption.

CONVENTIONAL METHODS OF MAXIMIZING WATER RE-USE

In order to maximize the re-use of water particularly in cooling applications, alkalinity and calcium concentrations need to be controlled at levels below those that would cause scaling of heat transfer surfaces. Although the exact concentration limits vary from plant to plant, the limit for calcium specified by cooling tower manufacturers is typically between 300 and 400 mg/L, and the alkalinity is often maintained below 100 mg/L in the cooling water loop. The industry achieves these limits by removing calcium and alkalinity either from fresh make-up water entering the plant or from a side stream of cooling tower blow-down that is subsequently returned to the cooling water loop.

CASE STUDIES OF SULF-IX PROCESS APPLICATION IN POWER GENERATION

TREATMENT OF POWER PLANT RAW MAKE-UP WATER

Figures 3A, 3B, and 3C, and Table 4 summarize the application of Sulf-IX in the pre-treatment of fresh make-up water prior to the use at a power plant, and present a comparison of Sulf-IX to conventional methods of treatment. The following describes the basis of the case study:

- Fresh water source is Colorado River water. The average quality of the river water was summarized by the US Department of Interior (US Geological Survey, 1996);
- Steam electric power plant output of 500 MWe and overall thermal efficiency of 34% was used as the basis for water flowrates;
- Ca concentration limit in cooling water loop of 300 mg/L was selected;
- Total alkalinity limit of 20 mg/L (CaCO₃ eq) was selected for the make-up water entering the cooling water loop to allow for a typical Cycle-of-Concentration of 4 without the need for blow-down

Figures 3A and 3B show the two conventional methods of pretreatment, i.e. acidification followed by de-carbonation (Figure 3A), and soda ash softening followed by acidification and de-carbonation (Figure 3B). Figure 3C shows the Sulf-IX treatment. As can be seen from Figure 3A, acidification followed by de-carbonation removes alkalinity but does not remove Ca. Soda ash softening followed by acidification, and the Sulf-IX process both remove not only alkalinity but also calcium. However, Sulf-IX is the only process that removes TDS.

Figure 3A – Fresh make-up water treatment by acidification and de-carbonation

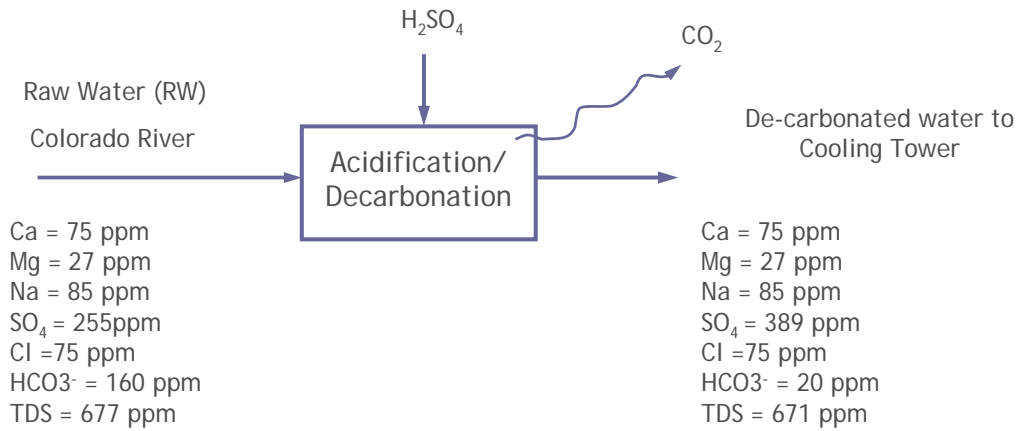


Figure 3B – Fresh make-up water treatment by acidification and de-carbonation

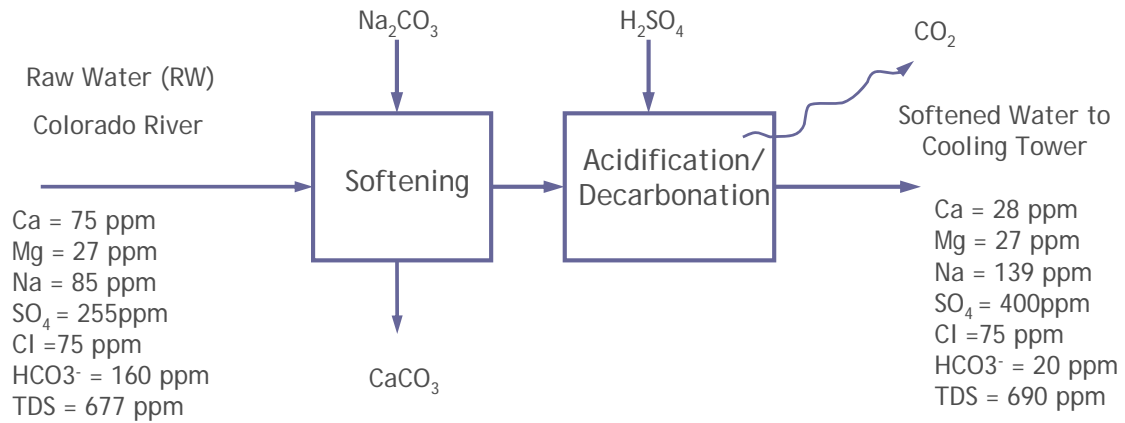


Figure 3C – Fresh make-up water treatment by Sulf-IX

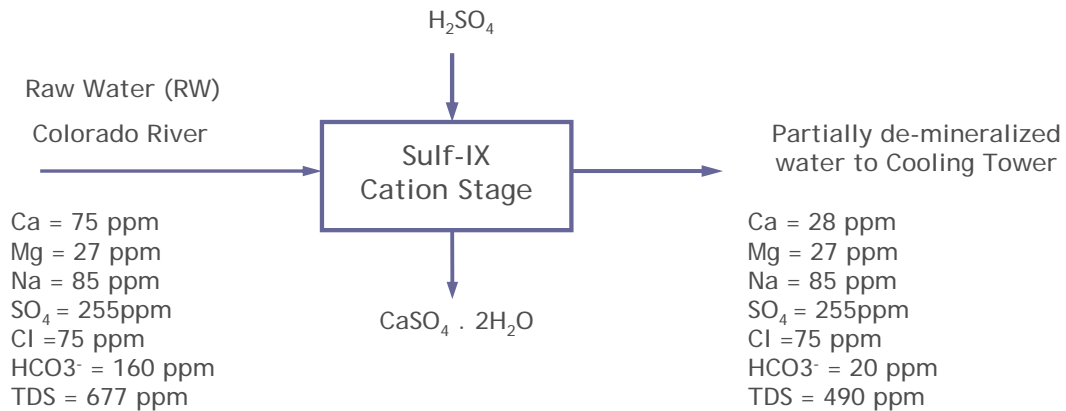


Table 4: Comparison of Sulf-IX to conventional methods of calcium and alkalinity control in fresh make-up water entering power plants

Item	Acidification	Conventional Softening followed by Acidification	Sulf-IX Calcium Removal	Benefit of Sulf-IX
Ca in Cooling Tower Make-up Water	75 mg/L	28 mg/L	28 mg/L	same benefit of lower calcium concentration as conventional softening
Alkalinity in Cooling Tower Make-up Water	20 mg/L	20 mg/L	20 mg/L	no benefit compared to other options
TDS in Cooling Tower Make-up Water	670 mg/L	690 mg/L	490 mg/L	lowest TDS of all options, Sulf-IX partially demineralizes make-up water
Ca concentration limit for Cooling Tower Blow-Down	300 mg/L	300 mg/L	300 mg/L	specification of cooling tower manufacturer
Maximum COC in Cooling Tower	4	10.7	10.7	same as conventional softening
TDS in Cooling Tower Blow-down	2,680 mg/L	7,383 mg/L	5,243 mg/L	lower TDS than conventional softening
Cooling Tower Blow-Down	490 m ³ /hr	151 m ³ /hr	151 m ³ /hr	same as conventional softening
Fresh Cooling Tower Make-up Water	1,958 m ³ /hr	1,619 m ³ /hr	1,619 m ³ /hr	same as conventional softening
Savings in fresh make-up water	0 m ³ /hr	339 m ³ /hr (800 million gallons/year)	339 m ³ /hr (800 million gallons/year)	same as conventional softening
Sulfuric Acid Consumption	137 mg/L	147 mg/L	137 mg/L	same as simple acidification, there is no residual alkali to neutralize
Soda Ash Consumption	0 mg/L	125 mg/L	0 mg/L	no need for costly sodium based alkali, eliminates the source of increased TDS
COMMODITY PRICING				
Soda Ash	\$350/dmt	\$350/dmt	\$350/dmt	\$350/dmt
Sulfuric Acid	\$280/mt 98%	\$280/mt 98%	\$280/mt 98%	\$280/mt 98%
Fresh Water	\$0.05/m ³ (\$0.19/1000 gallons)	\$0.05/m ³ (\$0.19/1000gallons)	\$0.05/m ³ (\$0.19/1000 gallons)	\$0.05/m ³ (\$0.19/1000gallons)
COMPARISON OF MAJOR OPERATING COST ITEMS				
Reagent Cost per Unit Volume Treated	\$0.039/m ³	\$0.085/m ³	\$0.039/m ³	same as acidification
Annual Reagent Cost	\$668,931	\$1,205,507	\$553,115	lowest reagent cost
Annual Fresh Water Cost	\$857,604	\$709,122	\$709,122	same as conventional softening
Total Reagents & Water Cost	\$1,526,535	\$1,914,629	\$1,262,237	lowest overall combined cost of reagents and water

As can be seen from Table 4, the Sulf-IX process option offers the lowest overall cost as it combines savings in fresh make-up water cost and low reagent cost. The net consumption of acid is lower for Sulf-IX than for the acidification option due to the fact that less water needs to be treated. The comparison of costs between acidification and softening options illustrates why some power plants do not use softening. The cost of fresh water is simply still too low to make the savings in the fresh make-up water cost outweigh the cost of softening chemicals. The fresh water cost is site specific and includes the cost of purchasing land for water rights or paying for water allocations, constructing and maintaining wells, pumps, and pipelines, and the cost of power for pumping. As an example, the cost of power for

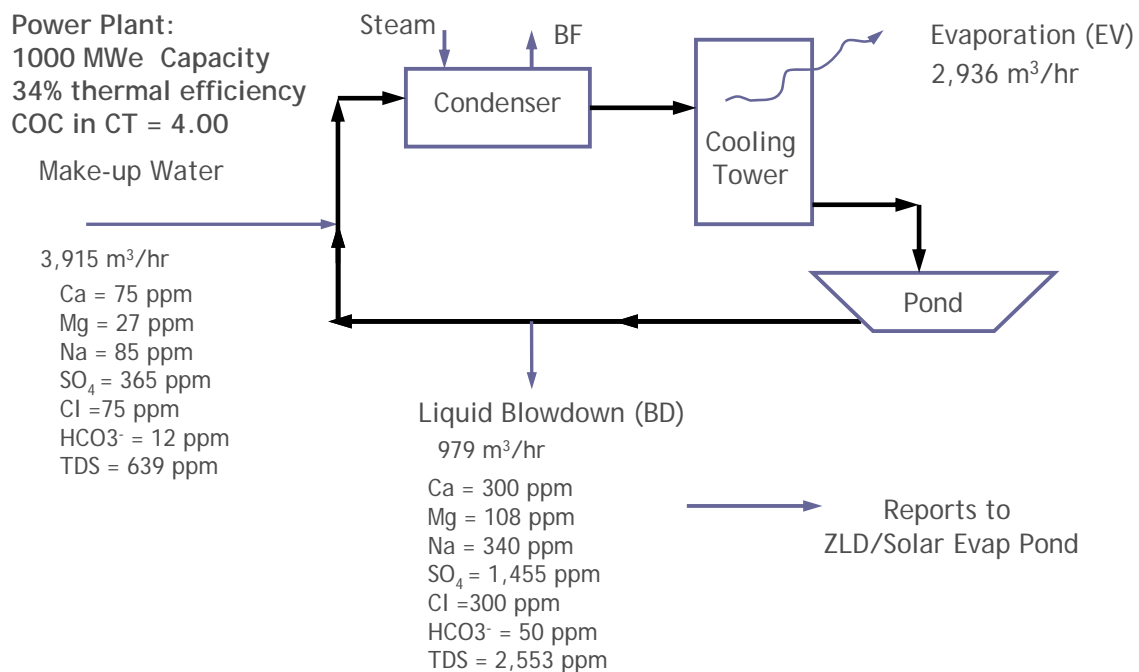
pumping water from a 100 m (300ft) deep well is approximately \$0.03/m³ (\$0.11/1000 gallons) and this cost increases proportionally to aquifer depth.

TREATMENT OF COOLING TOWER BLOW-DOWN

A case study of the Sulf-IX process applied to the treatment of cooling tower blow-down is summarized in Figures 4A and 4B and Table 5. The following describes the basis of the case study:

- Steam electric power plant capacity of 1,000 MWe and thermal efficiency of 34%;
- Ca limit in cooling water loop of 300 mg/L;
- Cooling make-up water composition as shown in Figures 4A and 4B with alkalinity reduced by pre-treatment.

Figure 4A: No TDS removal from treatment of cooling tower blow-down (typical)



The cooling tower blow-down compositions shown in Figures 4A and B illustrate that it would be difficult to treat these streams using membrane processes and expect a high water recovery and a reasonably low cost. The concentrations of calcium and sulfate in the blowdown streams are close enough to gypsum saturation to seriously limit the percentage water recovery. Furthermore, increased operating cost of membranes can be expected

due to the need for antiscalants, frequent cleaning, and possible replacement of the membranes.

As can be seen from Figures 4A, 4B and Table 5, the main source of all of the benefits brought about by the treatment of cooling tower blow-down by Sulf-IX is the reduction in the volume of the blow-down stream. The estimate of the reduction in the parasitic running power of 17 MW for a ZLD

system shown in Table 5 is based on the power consumption by evaporators used in thermo-mechanical ZLD systems outlined by Shaw (Shaw, 2008). According to Shaw the power consumption is approximately 70 kWh/1000 gallons (4.4kW/GPM of water recovered).

The Sulf-IX process application depicted in Figure 4B allows the cooling tower itself to operate as a light duty “evaporator” thus reducing the size of, or possibly even replacing, ZLD evaporators operating downstream of the cooling tower. The Sulf-IX process achieves this by removing scale forming species including Ca, HCO₃, and SO₄ from the cooling water in the form of solid products, thus accomplishing a true “solids blow-down” with minimal water loss, while allowing Na and Cl to build up in solution. Although many cooling towers are designed to operate on seawater, the increase in the TDS level in the cooling tower may be subject to permitting review. An

estimate of the gross annual operating cost savings created by the Sulf-IX process in this case study can be determined as follows:

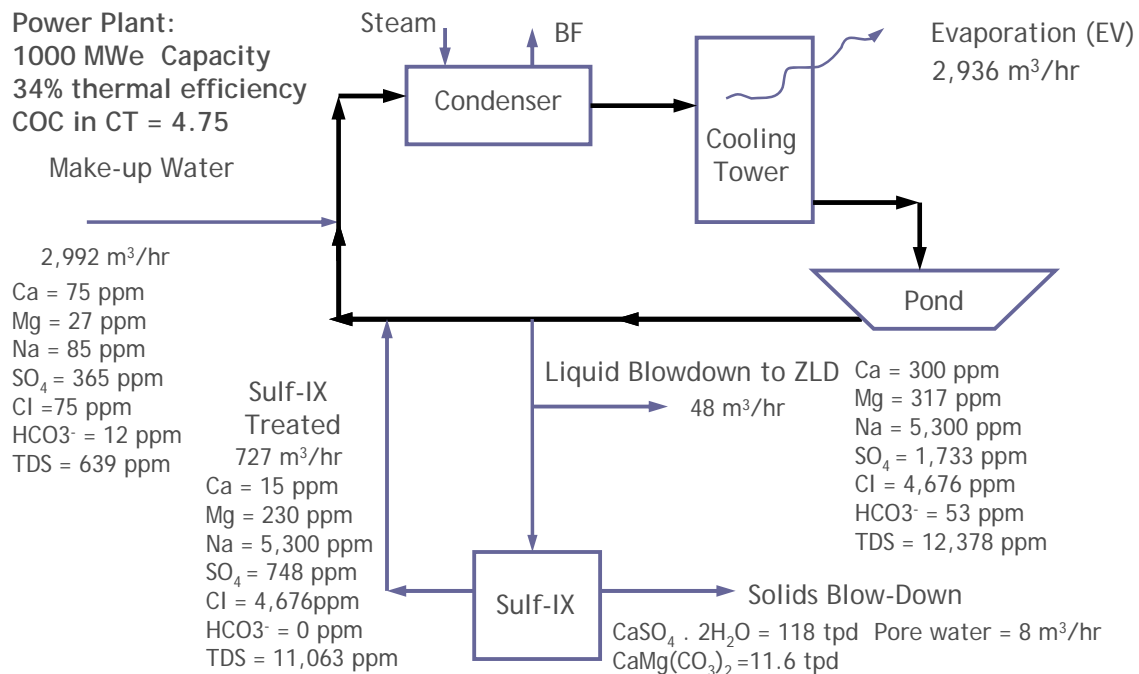
Power cost saving: 17 MW x \$80/MW x 24 x 365 = \$11.9 million/year;

Fresh water cost saving: 8 M m³/year x 0.05/m³ = \$0.4 million/year

Fresh water pre-treatment: 8 M m³/year x 0.04/m³ = \$0.3 million/year

The net annual operating cost savings will depend on the Sulf-IX process operating costs. The preliminary estimate of the Sulf-IX plant operating cost is \$7.5 M/year. However, on site piloting of the process would be required to confirm the process efficiency and resin life as affected by potential fouling by organic compounds or other compounds present in the cooling water loop, and by temperature of the water.

Figure 4B: Sulf-IX treatment of cooling tower blow-down



In addition to operating cost savings, there are major capital cost savings stemming from the fact that any ZLD system operating downstream of the cooling tower equipped with Sulf-IX treatment on the blow-down side stream will be much smaller and see much lower overall salt

throughput. The savings include the cost of constructing solar ponds and/or evaporator-crystallizer ZLD systems designed to operate at high temperature which forces equipment manufacturers to choose expensive materials of construction for the ZLD equipment.

Table 5: Summary of Benefits of Sulf-IX treatment of Cooling Tower Blow-Down

Item	No treatment of Cooling Tower Blow-Down	Sulf-IX treatment of Cooling Tower Blow-Down	Benefit of Sulf-IX
Maximum level of Calcium in Cooling Tower water	300 mg/L	300 mg/L	no benefit
Net volume of Blow-Down	979 m ³ /hr (4,307 GPM)	48 m ³ /hr (211 GPM)	Reduction in the size of ZLD (evap ponds or ZLD evaporators), power savings of up to 17 MW for ZLD evaporators operation. Capital cost savings for evaporators and/or ponds since much smaller units are required
Make-up water requirements	3,915 m ³ /hr (9.05 billion gallons/year)	2,992 m ³ /hr (6.92 billion gallons/year)	Savings in fresh water use, up to 8 M m ³ /year (2.1 billion gal/year) is conserved, protection of slow-recharge aquifers, maximum power generating capacity can be maintained during water shortage
Ca removed at ambient T, P	0 dmt/day	5 dmt/day	Produces clean gypsum that is not contaminated with heavy metals, boron, chlorides, or nitrates and can find end users
Mg removed at ambient T,P	0 dmt/day	1.5 dmt/day	Reduces power consumption by ZLD crystallizer
Ca load reduction for ZLD	0%	up to 35% of total Ca load	Reduces power consumption by ZLD crystallizer, reducing crystals dewatering circuit size
Mg load reduction for ZLD	0%	up to 42% of total Mg load	Reduces power consumption by ZLD crystallizer, reducing crystal dewatering circuit size

ASH POND WATER TREATMENT

Ash pond water is often not considered as water that could be re-used in cooling towers mainly because of elevated hardness and alkalinity that originate from the soluble components of ash (Evangelou, 1999). Similar to cooling tower blow-downs, ash pond waters are not a good target for the application of membranes due to concern with fouling and overall cost of treatment requiring several pre-treatment steps.

Tables 6 and 7 summarize the results of a case study of Sulf-IX process treating ash pond water from the Homer City power plant. The detailed analysis of the ash pond water was provided by the EPA (EPA, 2008). Table 6

shows the Sulf-IX plant feed and discharge composition. As can be seen from this table, the Sulf-IX plant achieves approximately 50% TDS reduction by selectively removing Ca and SO₄ from the ash pond water. In this case study, the design of the Sulf-IX plant design does not include the Mg removal circuit. Consequently, the removal of Mg is negligible. The small decrease in Mg concentration is mainly due to the deportment of a small amount of Mg into the gypsum products produced by the Sulf-IX plant. Table 7 summarizes reagent and power consumption and the cost of major consumables. As can be seen from Table 7, the total cost of the Sulf-IX plant excluding operating and maintenance labour is

approximately \$0.53/m³. This may seem like a high cost, however, it is actually relatively low cost in comparison with the alternative method of water recovery by ZLD evaporators which amounts to approximately \$1.5/m³ at the unit power cost of 0.08/kWh.

Table 6: Composition of feed and discharge from Sulf-IX plant treating ash pond water (Homer City ash pond water quality)

Water Constituent	Feed Concentration [mg/L]	Effluent Concentration [mg/L]
SO ₄	800	424
Ca	186	43
Mg	32	30
Na	106	106
Cl	90	90
TDS	1250	693

Table 7 Sulf-IX Operating Cost Summary

Operating Cost Item	Unit	Consumption
Lime consumption	dmt/day	424
Sulfuric acid Consumption	dmt/day	43
Running Power	kW	80
Consumable Pricing	Unit	US\$
Lime	dmt	180
Sulfuric acid	dmt	280
Power	kWh	0.08
Operating Cost	US\$/m ³	US\$/1000 gal
Lime	\$0.15	\$0.57
Sulfuric acid	\$0.29	\$1.08
Power	\$0.09	\$0.34
Total Operating Cost excluding Labor & Maintenance	\$0.53	\$1.99

CONCLUSIONS

In conclusion, three case studies of Sulf-IX process applied to the treatment of:

- 1) Fresh makeup water entering power plants;
- 2) Cooling tower blow-down; and
- 3) Ash pond water,

all showed that the Sulf-IX process offers a possibility of achieving a greater extent of water re-use at power plants compared to existing technologies while providing savings in water, power, and reagents along with capital cost savings for ZLD systems. Since most of the savings are in water and power, the economic incentive for adopting the Sulf-IX process is expected to improve as the price of electricity and water increases in the future. Finally, the case studies indicate that power plants relying on water sources with elevated hardness and TDS and/or plants located in areas of water scarcity would benefit the most from the adoption of the Sulf-IX process.

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