ION EXCHANGE

INNOVATIVE IX SYSTEMS FOR COST-EFFECTIVE INCREASE IN WATER REUSE IN POWER PLANTS

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 flue gas desulfurization (FGD) wastewater. Rising levels of calcium (Ca), magnesium (Mg), and sulfate (SO_4) limit the extent of water reuse by affecting the scaling potential of process water, while dissolved Ca, Mg chlorides increase the boiling point of waste liquors treated in zero liquid discharge (ZLD) evaporator-crystallizer systems, leading to increases in power consumption and capital cost of ZLD systems.

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 A summarizes the consumption of water by coal-fired power plants (1, 2). As can be seen from this table, and as noted in Reference 3, cooling water accounts for the largest portion of the overall consumption, followed by ash handling, and FGD scrubber make-up water. Cooling water consumption is composed of the following: 1. evaporative losses that are a function of the overall thermal efficiency of power plants; and 2. cooling tower blowdown, 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 A represent true water consumption as opposed to usage in that the water. The volumes listed in Table A 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 B summarizes limitations to water reuse.

Elevated levels of calcium hardness, SO_4^{2-}, TDS, and silica are among the most common limitations for water reuse 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. One example would be facilities that use Colorado River water, or water drawn from parts of the Ogallala aquifer. Power plant wastewaters that cannot be reused or discharged are directed to ZLD systems, which often consist of solar ponds for evaporation or salt crystallization, or mechanical evaporator-crystallizer units that crystallize salt at elevated temperature, and recover water through the condensate.

Process Description

Sulfate-removal process. A water treatment company's[a] sulfate-removal ion-exchange (IX) technology[b] has been developed specifically for the removal of TDS from hard waters with a high scaling potential, and elevated levels of sulfate. This method is a two-stage IX process, employing one cation and one anion resin placed in two separate circuits operating in series that achieve an overall partial demineralization of the feed by selectively removing calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulfate (SO_4^{2-}) from the plant feedwater.

The feed is first directed to the cation circuit operating with a strongly acidic cation (SAC) resin where Ca and Mg are

TABLE A
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 feedwater

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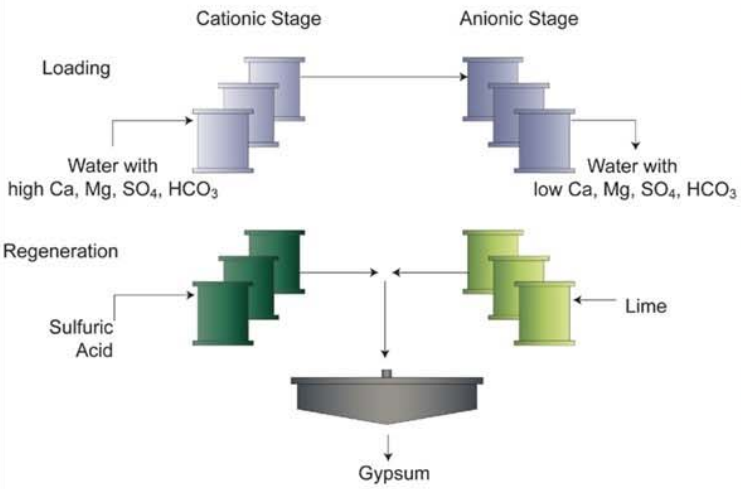

Figure 1. Sulfate-removal IX process schematic.

Figure 2. 25 m³/h sulfate-removal IX column.

removed. The effluent from the cation circuit is then directed to the anion circuit operating with a weakly basic anion (WBA) resin where sulfuric acid (H_2SO_4) produced in the cationic circuit is taken up by the resin. IX reactions during resin loading are identical to those used in conventional IX systems. The unique feature of the sulfate-removal IX process is the regeneration step that is accomplished by using H_2SO_4, 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

TABLE B
Limitations to Water Reuse

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_2SO_4 used for alkalinity control, sulfur from coal
Si	scaling/silica species	make-up water
TDS	air emissions PM_x/drift from cooling towers	all of the above (Ca, SO_4, Cl, and Si all contribute to TDS)

is then blended with the anionic gypsum to yield a final neutral gypsum product. The schematic of the sulfate-removal IX process is shown in Figure 1.

The unique feature of this 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. Equations 1 and 2 can describe the resin regeneration reactions taking place in the cation and anion stages. Equation 1 demonstrates cation resin regeneration (100% recycle of regenerant). Equation 2 illustrates anion resin regeneration (100% recycle of regenerant).

$$CaSO_4.2H_2O(aq) + Ca^{2+}(aq) + 2H^+(aq) + 2SO_4^{2-}(aq) + 2R_f\text{-}Ca(resin) + 2H_2O \text{ ----> } 2R_f\text{-}H(resin) + Ca^{2+}(aq) + SO_4^{2-}(aq) + 2\ CaSO_4.2H_2O(s) \quad \text{Eq. 1}$$

$$R_f\text{-}H_2SO_4(resin) + CaSO_4.2H_2O(aq) + 2Ca^{2+}(aq) + 2OH^-(aq) + SO_4^{2-}(aq) \text{ ----> } R_f + Ca^{2+}(aq) + SO_4^{2-}(aq) + 2\ CaSO_4.2H_2O(s) \quad \text{Eq. 2}$$

Where:
(s) = solid
(aq) = solution
(resin) = resin/gel phases
R_f = the resin functional groups.

The formula of undissociated gypsum species $CaSO_4.2H_2O$ (aq) is included on both sides of Equations 1 and 2 in order to highlight the fact that as a result of the regenerant recycle, the regeneration of resins in the sulfate-removal IX takes place under gypsum saturation conditions in the bulk of solution.

Magnesium is removed together with Ca in the cation stage of the sulfate-removal 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 $CaMg(CO_3)_2$ or $Mg(OH)_2$ by reacting with carbon dioxide (CO_2), or lime.

Figure 2 shows the small demonstration pilot unit of the sulfate-removal IX operating at 200 liters per hour (L/h) (55 gallons per hour [gph]) of continuous feed, and a large unit operating at 25 cubic meters per hour (m^3/h) (110 gallons per minute [gpm]).

If there is bicarbonate alkalinity present in the feedwater, CO_2 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 sulfate-removal IX can be summarized as follows:

- The process operates on hard scaling water, and in the presence of suspended solids without any pretreatment 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.
- The process achieves very high water recovery since the only water lost in the process is the pore water contained in the solids products.
- The process has lower operating costs than membrane systems, or conventional IX systems because of inexpensive regenerants, and low power consumption.

Conventional Methods of Maximizing Water Reuse

In order to maximize the reuse 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 milligrams per liter (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

TABLE C
Comparison of Sulfate-Removal IX to Conventional Methods of Calcium and Alkalinity Control*

Item	*Acidifcation*	*Conventional Softening followed by Acidification*	*Sulfate IX Calcium Removal*	*Benefit of Sulfate-Removal 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 blowdown	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 blowdown	2,680 mg/L	7,383 mg/L	5,243 mg/L	lower TDS than conventional softening
Cooling tower blowdown	490 m^3/h	151 m^3/h	151 m^3/h	same as conventional softening
Fresh cooling tower make-up water	1,958 m^3/h	1,619 m^3/h	1,619 m^3/h	same as conventional softening
Savings in fresh make-up water	0 m^3/h	339 m^3/h (800 million gallons/ year)	339 m^3/h (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$	$0.05/$m^3$ ($0.19/1000gallons)	$0.05/$m^3$	$0.05/$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 freshwater 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

*In fresh make-up water entering power stations.

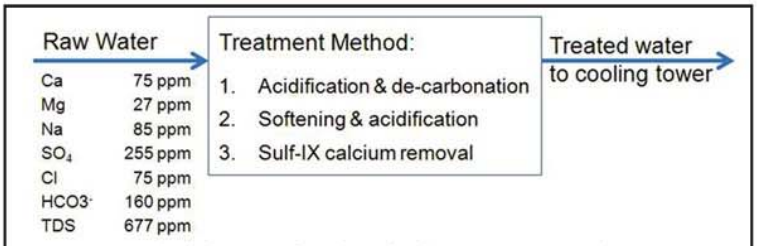

Figure 3. Simple feed process flowsheet of make-up water case study treatment options.

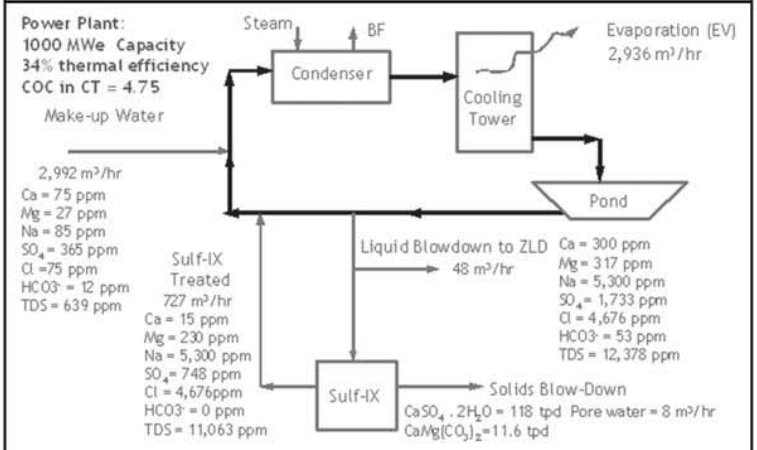

Figure 4. Sulfate-removal IX treatment of cooling tower blowdown.

water entering the plant, or from a side stream of cooling tower blowdown that is subsequently returned to the cooling water loop.

Case Studies

Treatment of power plant raw make-up water. Figure 3 and Table C summarize the application of sulfate-removal IX in the pretreatment of fresh make-up water prior to the use at a power plant, and present a comparison of this IX process and 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 U.S Department of Interior (4).
- Steam electric power plant output of 500 megawatt electrical (MWe), and the overall thermal efficiency of 34% were 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 ($CaCO_3$ 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 blowdown.

Figure 3 shows a simplified process flowsheet with three treatment systems that have been vompared. Acidification, followed by decarbonation removes alkalinity, but does not remove Ca. Soda ash softening, followed by acidification, and the sulfate-removal IX process both remove not only alkalinity, but also calcium. However, the sulfate-removal IX is the only process that also removes TDS.

As can be seen from Table C, the sulfate-removal 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 the sulfate-removal 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-meter (m) (300-foot[ft]) deep well is approximately \$0.03/m³ (\$0.11/1,000 gallons), and this cost increases proportionally to aquifer depth.

Treatment of cooling tower blowdown. A case study of the sulfate-removal IX process applied to the treatment of cooling tower blowdown is summarized in Figure 4 and Table D. 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 Figure 4 with alkalinity reduced by pretreatment.

The cooling tower blowdown compositions shown in Figure 4 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, the 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 4 and Table D, the main source of all of the benefits brought about by the treatment of cooling tower blow-down by the sulfate-removal IX is the reduction in the volume of the blowdown stream. The estimate of the reduction in the parasitic running power of 17 MW for a ZLD system shown in Table D is based on the power consumption by

evaporators used in thermo-mechanical ZLD systems outlined by Shaw (5). According to Shaw, the power consumption is approximately 70 kilowatt hours per 1,000 gallons (kWh/1,000 gal (4.4 kilowatts per gallon per minute [kW/gpm] of water recovered).

The sulfate-removal IX process application depicted in Figure 4 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 sulfate-removal IX process achieves this by removing scale-forming species, including Ca, bicarbonate (HCO_3), and SO_4 from the cooling water in the form of solid products, thus accomplishing a true "solids blowdown" with minimal water loss, while allowing sodium (Na) and chlorine (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 maybe subject to permitting review. An estimate of the gross annual operating cost savings created by the IX process discussed 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

Freshwater cost saving: 8 million (M) m^3/year x 0.05/ m^3 = $0.4 million/year

Freshwater pretreatment: 8 M m^3/year x 0.04/ m^3 = $0.3 million/year

The net annual operating cost savings will depend on the sulfate-removal IX process operating costs. The preliminary estimate of the plant operating cost is $7.5 M/year for this type of IX process. 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 water temperature.

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 the sulfate-removal IX treatment on the blowdown 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.

Ash pond water is often not considered as water that could be reused in cooling towers, mainly because of elevated hardness and alkalinity that originate from the soluble components of ash (6). Similar to cooling tower blowdown, ash pond waters are not a good target for the application of membranes because of concerns with fouling, and the overall treatment cost, including several pretreatment steps.

Tables E and F summarize the results

TABLE D
Summary of Benefits of Sulfate-Removal IX Treatment of Cooling Tower Blowdown

Item	*No Treatment of Cooling Tower Blowdown*	*Sulfate Removal IX Treatment of Cooling Tower Blowdown*	*Benefit of Sulfate-Removal IX*
Maximum level of calcium in cooling tower water	300 mg/L	300 mg/L	no benefit
Net volume of blowdown	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 (2.1billion 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 endusers.
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.

of a case study using the sulfate-removal IX process to treat ash pond water from the Homer City, Pa., power plant. The detailed analysis of the ash pond water was provided by the EPA (1). Table E shows the sulfate-removal IX plant feed and discharge composition. As can be seen from this table, the IX plant achieves approximately 50% TDS reduction by selectively removing Ca and SO_4 from the ash pond water.

In this case study, the design of the sulfate-removal plant design does not include the Mg removal circuit. Consequently, the removal of Mg is negligible. The small decrease in Mg concentration is mainly because of the deportment of a small amount of Mg into the gypsum products produced by the sulfate-removal IX plant.

Table F summarizes reagent and power consumption and the cost of major consumables. As can be seen from Table F, the total cost of the sulfate-removal IX plant, excluding operating and maintenance labor is approximately \$0.53/m^3. 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/m^3 at the unit power cost of 0.08/kWh.

Conclusions

In conclusion, three case studies of the sulfate-removal IX process all showed that a technology like the sulfate-removal IX process offers a possibility of greater water reuse at power plants, while also providing savings in water, power, reagents, and the capital costs for ZLD systems. This is based on the case studies that examined treatment of fresh makeup water entering power plants, cooling tower blowdown, and ash pond water. Since most of the savings are in water and power, the economic incentive for adopting this type of process is expected to improve as the price of electricity and water increases in the future.❑

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Endnotes

[a]BioteQ Environmental Technologies Inc. of Vancouver, B.C., is the water treatment company referred to in the text.
[b]Sulf-IX™ is the sulfate-removal ion-exchange technology referred to in the text. BioteQ Environmental Technologies is the developer of Sulf-IX™.

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TABLE E
Composition of Feed and Discharge from Sulfate-Removal IX Plant Treating Ash Pond Water*

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

*Homer City ash pond water quality

TABLE F
Sulfate-Removal 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$/m³	US$/1000 gal
Lime	$0.15	$0.57
Sulfuric acid	$0.29	$1.08
Power	$0.09	$0.34
Total operating cost, excluding labor and maintenance	$0.53	$1.99

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