Chemistry of FGD Blowdown

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ABSTRACT

As limits for metals are lowered and new parameters regulated, the complexity and cost of treatment to meet these low limits and add on treatment technology has made zero liquid discharge a more viable option for flue gas desulfurization blowdown. Coal and blowdown chemical make-up impacts the water chemistry and treatment technologies. This paper discusses the water chemistry associated with concentrating and crystallizing blowdown and presents a commercial model used in the evaluation.

BACKGROUND

Past applications of zero liquid discharge (ZLD) systems in the power industry have been confined typically to cooling tower blowdown in areas where water was scarce, in terms of either source waters or discharge locations for wastewater. The ZLD designs for these wastewaters generally considered water chemistries involving the concentration of sodium chloride. Because sodium chloride can be crystallized at a relatively low temperature, ZLD of cooling tower blowdown treatment is simpler than ZLD of flue gas desulfurization (FGD) blowdown water. This is because limestone-based FGD systems produce waters with high concentrations of calcium and magnesium chloride, which require very high temperatures to crystallize.

Presently, ZLD is becoming a more viable option for discharge of complex industrial wastewater. Drivers for ZLD include lowering of water quality standards for metals; implementation of chloride, sulfate, and total dissolved solids (TDS) water quality standards; as well as scarcity of water resources. The Environmental Protection Agency (EPA) is looking to ZLD, using evaporators and crystallizers, as a viable treatment technology for FGD blowdown, as noted in their report entitled *Steam Electric Power Generating Point Source Category: Final Detailed Study Report* (EPA, 2009).

ZLD treatment of FGD blowdown is complex, as the wastewater has high levels of calcium and magnesium chloride and sulfate. Coal quality impacts both the resulting FGD blowdown and the disposal alternatives for the final brine. The resulting FGD blowdown water chemistry drives the water recovery, solids formation, and applicable ZLD technologies. This paper presents approaches to evaluating the coal and FGD blowdown, and modeling evaporators and crystallizers using the approaches developed by CH2M HILL. It also outlines the effects of weightfractions of inorganic salts (calcium, magnesium, chloride, and sulfate) on final brine recovery.

INTRODUCTION

Due to the complex water chemistry of FGD blowdown, a tool that can predict the impacts of evaporation and crystallization is critical to understand potential impacts of the water chemistry. OLI System's StreamAnalyzer™ has been effective in evaluating water chemistry in evaporation/crystallization processes including modeling boiling point rise, solids formed, and potential scaling issues. StreamAnalyzer™ is an equilibrium-based, multi-phase simulation of electrolyte systems produced by OLI Systems, Inc. This software can simulate solutions under evaporator and crystallizer conditions, including temperature, pressure, and ionic strength.

We have developed an Excel[™]-based mass balance tool that we couple with StreamAnalyzer[™] to evaluate alternative water chemistries and ZLD alternatives. This model requires the manual transfer of data between Excel and StreamAnalyzer[™]. To automate this process, the water chemistry simulation engine and equilibrium parameters developed by OLI was paired with the process simulation capabilities of Aspen Plus[™] (developed by Aspen Technology, Inc.) using Aspen OLI[™]. The addition of process simulation enhances modeling by simultaneously accounting for recycle streams, complex chemistry, and the heat balance around the system.

It is also critical to understand how changes in coal quality impact the composition and volume of FGD blowdown. Coal quality also impacts gypsum and fly ash production, which is significant because both can be sold commercially or used to cost-effectively dispose of evaporator brine through mixing and landfilling. We have developed a tool to estimate FGD wastewater volumes, gypsum, and fly ash quality. To determine these factors, the tool uses information collected for typical coal qualities found in the U.S., along with chloride tolerances for the FGD system.

APPLICATION TO FGD BLOWDOWN

We applied the aforementioned models to evaluate evaporation and crystallization of FGD blowdown. StreamAnalyzer[™] has been the core technology used to evaluate the complex nature of these processes. This software has the capacity to modify variables such as pH, temperature, composition, and pressure; as well as the ability to model the vapor, liquid, and solid phases. These features allow it to simulate the conditions of a multitude of processes, including estimating chemical usages and determining the resulting water chemistry.

A wastewater profile is first generated using water chemistry data collected from the FGD blowdown at the location being considered for treatment. StreamAnalyzer™ is used to check the analytical data for charge neutrality, and then balance the charges. The balanced water chemistry is input into an Excel-based mass balance spreadsheet. Figure 1 shows a portion of the integrated mass balance generated using our spreadsheet tool. When pretreatment is warranted, we have used the software to evaluate operating set-points. Stripping inert gases and chemical softening have been evaluated using this modeling approach to identify operational information such as pH, temperature, acidification, and neutralization requirements. This operational information, along with flows and solids compositions, is linked to separate worksheets that size the equipment for the system (Figure 2). This

information, in turn, is used to generate estimates for capital expenditures and operating expenses. As shown in Figure 2, the equipment sizing can be modified based on individual preferences for capacity and redundancy.

Determination of evaporation/crystallization equipment is based on the requirements for the final stream (either a concentrated brine or salt cake). If the desired end point is formation of a salt cake for disposal, the crystallization and dewatering equipment are selected based on the type of solid expected to be formed and potential scaling or fouling issues. StreamAnalyzer™ also can determine boiling point rise of the stream to evaluate whether concentration using a vapor compression evaporator is feasible. Conventional compressors are limited to a pressure where steam condenses at around 226° F. The practical limit of heat exchangers is about 8°F, which limits the brine boiling point rise to 5.5 to 6.5°F. Vapor compression evaporators are more energy-efficient than steam evaporators and are typically preferred, depending on the water chemistry. StreamAnalyzer™ is also used to determine the type and relative quantity of solids formed when the water is concentrated. Understanding the relative amounts of solids in the brine is helpful in evaluating antiscalant selection, seeding, brine transfer and holding, and equipment selection. Alternatives for ZLD systems and the corresponding water chemistry impacts are discussed further in later sections.

Figure 1: Portion c	of Integrated	Mass Balance	Spreadsheet Too	I
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			Figu	re 1: Po	rtion of	Integr	ated N	1ass Ba	lance S	preads	heet To	loc			
	U8 🔻 💽	Jx	=E8							<u> </u>					
	A	В	C	D	E	F	G	Н		J	K	L	М	N	(
1	ZLD Full Mass Bala	nce													
2	Component	Units	MW												
						H ₂ SO ₄	Deaerator					Caustic to	Evaporator	Evaporator	
					Raw Water	Added	Influent	Caustic for	Scale		Evaporator	keep pH at	Steam and	Cool	Evap
3	Stream Name			Raw Water	(SA)	(SA)	(SA)	pH 7.5	Inhibitor	Antifoam	Feed (SA)	6.5	Mist (SA)	Distillate	Blow
4								Physic	al Propertie	es					
5	pН	su		7.0	6.8		5.5				7.5				
6	Temperature	٩F		60.0	60.0		60.0				207.0		217.7	65.0	
7	Temperature	°C		15.6	15.6		15.6				97.2		103.2	18.3	
8	Solution Density - SA	g/ml		1.004	1.004	1.840	1.004	1.525			0.964	1.525	0.954	0.998	
9	Solids Density - SA	g/ml		3.234	3.234		2.941				2.970				
10	Slurry Density	g/ml		1.004	1.004		1.004				0.966			0.998	
11								Volum	netric Flows	5					
12	Flow	gpm		931.6	932.1	0.015	932.2	0.106	0.009	0.009	970.0	0.205	960.1	917.5	
13	Flow	MGD		1.342	1.342		1.342				1.397		1.383	1.321	
14	Flow	l/min		3521.5	3528.1	0.055	3528.3	0.40			3671.3	0.78	3634.1	3472.9	
15	Flow-liquid only	l/min			3528.0		3528.1				3669.9		3634.1	3472.9	
16	Solutions - SA	m ³ /min			3.5280		3.5281				3.6696				
17	Solids - SA	m ³ /min			0.00003		0.0001				0.0014				
18	Dewatered Sludge	cf/day													
19								Mass F	lows (Metri	c)					
20	Total - SA	Kg/min		3540.78	3540.78	0.10	3540.88	0.61			3541.39	1.19	3466.96	3466.96	
21	Solutions	Kg/min		3540.67	3540.67		3540.70				3537.18		3466.96	3466.96	
22	Water	Kg/min		3517.40	3517.40	0.01	3517.41	0.31			3517.47	0.59	3466.94	3466.94	
23	TDS (as compounds)	Kg/min			23.28		23.30				19.71		0.02	0.02	
24	TDS (as ions only)	Kg/min		21.31	20.25		20.20				16.32		0.02	0.02	
25	TSS	Kg/min		0.11	0.11		0.18				4.20		0.00	0.00	
26	Cations				/						/				
14	🔹 🕨 📃 ZLD Full Mass B	alance 🖉 Zl	.D Mass Ba	alance for PFD	🔍 Unit Sizing	📝 Equip	ment List 🏒	Cost Estima	te 🖌 Annu	alized Cost 📿	Electrical L	oad 🔬 Chen	nical usagi 🔳 🚛		

Figure 2: Portion of Integrated Equipment Sizing from Spreadsheet Tool

Partial ZLD: Equipment	Sizina								
User Kev									
,	Referenced fro	m full mass balance	sheet						
	Local Equipme	ent Preferences							
	Universal Equi	Universal Equipment Preferences (Default)							
5	Adjustable valu	le used for calculation	ns (e.a. pipe lenati	h), enter new value if known					
User Input for Universal Redu	undance and Capa	citv							
	Quantity	Percent Capacity	Quantity						
Type of Equipment	Installed	Each	Purchased						
Pump(s)	2	100%	2						
Tank(s)	1	100%	1						
Evaporator System(s)	2	100%	2						
		1							
Equipment Sizing	1								
Note: Universal preferences in	table above are defa	ut. Leave local equip	ment quantities ar	d capacities blank to					
defeult to universal preferences	Local preferences	override universal pre	ferences, if entered	d.					
delault to universal preferences.	. Local preletences								
delault to universal preferences.	. Local preferences								
delault to universal preierences.	Equipment								
Item	Equipment Quantity	Value	Units	Notes					
Item ZLD Feed Pump	Equipment Quantity	Value	Units	Notes					
Item ZLD Feed Pump Type	Equipment Quantity	Value	Units	Notes					
Item ZLD Feed Pump Type Purchased	Equipment Quantity	Value	Units	Notes					
Item ZLD Feed Pump Type Purchased Installed	Equipment Quantity	Value Pump	Units	Notes					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity	Equipment Quantity	Value Pump	Units	Notes					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total)	Equipment Quantity	Value Pump 300	Units each gpm	Notes					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (each)	Equipment Quantity	Value Pump 300 300	Units each gpm gpm	Notes					
Item Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (each) Pipe Velocity	Equipment Quantity	Value Pump 300 300 6.68	Units each gpm gpm feet per second	Notes					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (each) Pipe Velocity Pipe Diameter	Equipment Quantity	Value Pump 300 300 6.68 6	Units each gpm gpm feet per second in	Notes Notes Default value, enter new value if known Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (each) Pipe Velocity Pipe Diameter Hazen Williams Constant	Equipment Quantity	Value Pump 300 300 6.68 6 150	Units each gpm gpm feet per second in	Notes Notes					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (each) Pipe Velocity Pipe Diameter Hazen Williams Constant v = flow velocity (ft/s)	Equipment Quantity	Value Pump 300 300 6.68 6 150 3.34	Units each gpm gpm feet per second in	Notes Notes Default value, enter new value if known Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (Total) Pipe Velocity Pipe Diameter Hazen Williams Constant v = flow velocity (ft/s) f = friction head loss	Equipment Quantity	Value Pump 300 300 6.68 6 150 3.34 0.62	Units each gpm gpm feet per second in ft/100 ft	Notes Notes Default value, enter new value if known Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (Total) Design Flow (each) Pipe Velocity Pipe Diameter Hazen Williams Constant v = flow velocity (ft/s) f = friction head loss Pipe Length	Equipment Quantity	Value Pump 300 300 6.68 6 150 3.34 0.62 500	Units each gpm gpm feet per second in ft/100 ft ft	Notes Notes Default value, enter new value if known Default value, enter new value if known Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (each) Pipe Velocity Pipe Velocity Pipe Diameter Hazen Williams Constant v = flow velocity (ft/s) f = friction head loss Pipe Length Minor Losses	Equipment Quantity	Value Pump 300 300 6.68 6 150 3.34 0.62 500 1,000	Units each gpm gpm feet per second in f/100 ft ft ft	Notes Notes Default value, enter new value if known					
Item Item Item Item Item Item Item Item	Equipment Quantity	Value Pump 300 300 6.68 6 300 3.34 0.62 500 1,500 1,000 1,500	Units each gpm gpm feet per second in ft/100 ft ft ft ft	Notes Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (Total) Distance Pipe Velocity Pipe Velocity Pipe Velocity Fipe Velocity fi = friction head loss Pipe Length Minor Losses Total Equivalent Length Head Loss	Equipment Quantity	Value Pump 300 300 6.68 6 150 3.34 0.62 500 1,000 1,500 9,3	Units each gpm gpm feet per second in ft/100 ft ft ft ft ft	Notes Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (Total) Diseign Flow (each) Pipe Diameter Hazen Williams Constant v = flow velocity (ft/s) f = friction head loss Pipe Length Minor Losses Total Equivalent Length Head Loss Elevation Difference	Equipment Quantity	Value Pump 300 300 6.68 6 150 3.34 0.62 500 1,000 1,500 9.3 20	Units each gpm gpm feet per second in ft/100 ft ft ft ft ft ft ft ft	Notes Default value, enter new value if known					
Item Ltem Ltem LD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (total) Design Flow (each) Pipe Velocity Pipe Diameter Hazen Williams Constant v = flow velocity (ft/s) f = friction head loss Pipe Length Minor Losses Total Equivalent Length Head Loss Elevation Difference Total Head	Equipment Quantity	Value Pump 300 300 6.68 6 6 150 3.34 0.62 500 1,000 1,500 9.3 20 20 29.3 29.3	Units each gpm gpm feet per second in ft/100 ft ft ft ft ft ft ft ft ft ft	Notes Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (Total) Distribution (Total) Distribution (Total) Pipe Velocity Pipe Diameter Hazen Williams Constant V = flow velocity (ft/s) f = friction head loss Pipe Length Minor Losses Total Equivalent Length Head Loss Elevation Difference Total Head Water Horsepower	Equipment Quantity	Value Pump 300 300 6.68 6 3.34 0.62 500 1,500 1,500 1,500 9,3 20 29,3 2,2,2	Units each gpm gpm feet per second in ft/100 ft ft ft ft ft ft ft ft HPw	Notes Default value, enter new value if known I HP=33,000 ft-lbs/minute					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (Total) Distance Pipe Velocity Pipe Diameter Hazen Williams Constant v = flow velocity (ft/s) f = friction head loss Pipe Length Minor Losses Total Equivalent Length Head Loss Elevation Difference Total Head Water Horsepower Assumed Efficiency	Equipment Quantity	Value Pump 300 300 6.68 6 150 3.34 0.62 500 1,500 1,500 1,500 2,9.3 20 2,2.2 2,2 2,2 2,66%	Units each gpm gpm feet per second in ft/100 ft ft ft ft ft ft ft ft ft HPw	Notes Default value, enter new value if known					
Item ZLD Feed Pump Type Purchased Installed Percent Capacity Design Flow (Total) Design Flow (Total) Distance Pipe Diameter Hazen Williams Constant v = flow velocity (ff/s) f = friction head loss Pipe Length Minor Losses Total Equivalent Length Head Loss Elevation Difference Total Head Water Horsepower Assumed Efficiency Total HP	Equipment Quantity	Value Pump 300 300 300 6.68 6 150 3.34 0.62 500 1,000 1,500 9.3 20 29.3 2.2 66% 3.44 3.44	Units each gpm gpm feet per second in ft/100 ft ft ft ft ft ft ft ft ft ft ft HPw HP	Notes Default value, enter new value if known 1 HP=33,000 ft-lbs/minute Default value, enter new value if known					

In addition, materials of construction must be carefully selected using the water chemistry characteristics of the concentrated stream to evaluate potential corrosion issues.

PREDICTING WATER CHEMISTRY OF FGD BLOWDOWN

The characteristics of FGD blowdown will vary depending on the chloride concentration that drives the number of times the water can be concentrated. The magnesium-to-calcium ratio of the limestone will drive the amount of magnesium in solution. The sulfur-to-chlorine ratio of the coal will determine whether the blowdown will be dominated by sulfate or chloride. A high-chloride coal combined with a high-calcium limestone will produce a blowdown high in calcium and chloride and low in magnesium and sulfate. A high-sulfur coal and high-magnesium limestone will produce a lowcalcium, high-magnesium sulfate and chloride blowdown. Concentration of FGD scrubber blowdown precipitates calcium sulfate and produces a stream that is primarily calcium and magnesium chloride. The general effect on water recovery in a ZLD system from the magnesium content of the limestone, and chloride and sulfur content of the coal is shown in Table 1.

Coal Major Species Relative Limestone Formed in Brine Cl Level S Level Mg Level Flow ZLD Low Low Low Ca, Cl Low Low Low High Mg, Cl, SO₄ Medium Ca, SO₄, Cl Low High Low Low High High Mg, SO₄, Cl Medium Low High Low Low Ca, Cl Medium High Low High Mg, Cl, SO₄ High Ca, SO₄, Cl High High Low High High High High Mg, SO₄, Cl Highest

Table 1: Water Chemistry Effects On Brine Flow

Notes: Mg-Magnesium; Ca-Calcium; Cl-Chloride; S-Sulfur; SO₄- Sulfate

Coal quality affects gypsum and fly ash production, in addition to impacting the water chemistry of FGD blowdown. Fly ash is composed of particles, either incombustible or not consumed, formed when the coal is burned and transferred by exhaust gases. The production of gypsum, a byproduct of calciumbased scrubbers, is based on the sulfur content of the coal. Both gypsum and fly ash often present cost-effective disposal methods for ZLD concentrated brine, which is used for wetting and landfilling the products, minimizing energy and equipment requirements for ZLD. However, since some plants sell their fly ash and gypsum, committing to this disposal method may negatively impact operating costs.

As shown on Figure 3, our spreadsheet tool estimates FGD wastewater volumes as well as gypsum and fly ash quality. This approach considers typical coal qualities found in the U.S., including sulfur, chloride, and ash contents. Once a coal has been selected, operational setpoints are used to estimate the volume of water generated, including chloride levels in the FGD blowdown. Chloride levels in blowdown can vary from 3,000 to 35,000 milligrams per liter (mg/L). Depending on the metallurgy of the scrubber with regard to its ability to handle higher chloride concentrations, a facility might be able to mix the blowdown with the landfilled solids, negating the need for further treatment. Fly ash production is based on the coal's characteristics, while gypsum production is based on the sulfurremoval efficiency and grade of gypsum, dependent upon the final fate (landfill or commercial). The tool also estimates the volume of water required to wet the ash and gypsum for disposal in a landfill. The tool does not predict calcium, magnesium, or sulfate concentrations for the final water.

The quality of the limestone used in the scrubbers also impacts the FGD blowdown chemistry. Limestone with a high magnesium concentration is unfavorable, due to the risk of magnesium hydroxide scaling at the elevated evaporation temperatures.

ZLD ALTERNATIVES AND WATER CHEMISTRY IMPACTS

Evaporators and crystallizers are typical equipment used to develop a ZLD system. Each has multiple types; some variations include the method for vaporizing the wastewater. Chemical makeup of the FGD blowdown influences the selection and configuration of equipment, which in turn affects the level of vaporization and the final concentrated solution. A few key technologies and their impacts on water chemistry are discussed in the following sections.

"Waste" Water Bleed										
Chloride in FGD for Zero Discharge	ppm	20,338	32,301							
Disposable Grade Gynsum										
Chloride Concentration in EGD Bleed	nnm	5000	10000	15000	20000	25000	30000	35000	40000	45000
Bleed Sp. Gr (Conservative Assumption)	ppin	1 05	1.06	1 07	1.08	1 09	1 1	1 11	1 12	1 13
Bleed Density (Conservative Assumption)	lh/cu ft	65.5	66.1	66.8	67.4	68.0	68.6	69.3	69.9	70.5
Cl Removed by EGD	tnh	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cl Leaving with Gynsum	tnh	0.0	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3
Cl to be Removed in WWT Bleed	tph	0.1	0.1	0.0	0.0	0.0	-0.1	-0.1	-0.1	-0.2
Bleed to WWTS. Mass Flow Rate	tph	19	6	2	0	-1	-2	-3	-3	-3
Bleed to WWTS, Volume Flow Rate	cu.ft/h	584	195	66	3	-34	-59	-75	-88	-97
Bleed to WWTS, Volume Flow Rate	gpm	73	24	8	0	-4	-7	-9	-11	-12
	01									
Ash Wetting Option (and Disposable Grade Gypsum)										
Fly Ash Removed in ESP or FF	tph	20	20	20	20	20	20	20	20	20
Wetting Water for Dust Suppression (% Wt of Fly Ash)	%	15	15	15	15	15	15	15	15	15
Water needed for dust suppression	tph	3	3	3	3	3	3	3	3	3
Water needed for dust suppression	cu.ft/h	93	92	91	91	90	89	88	87	87
Water needed for dust suppression	gpm	12	12	11	11	11	11	11	11	11
Bleed to WWTS after Ash Wetting Useage, Volume Flow Rate	gpm	61	13	-3	-11	-15	-18	-20	-22	-23

Figure 3: Portion of FGD Blowdown Predictions from Spreadsheet Tool

SOFTENING PRETREATMENT - Depending on the nature of the FGD wastewater, pretreatment may be required to: remove compounds that are problematic to concentrate or result in extreme acidic conditions in the evaporator/ crystallizer, reduce scaling potential, change the chemistry of the crystallizer, or concentrate the stream prior to evaporation/crystallization. Softened water generally can be concentrated further, using less energy, than original waters. Softening removes calcium and magnesium in the water, replacing them with sodium. Sodium chloride is easier, and requires much lower temperatures, to crystallize than calcium or magnesium chloride. Formation of magnesium hydroxide also can cause a more difficult scaling problem than calcium sulfate. The use of softening pretreatment to achieve more efficient ZLD systems is generally at the expense of high operating costs for the additional chemical consumption and solids generation. Figure 4 shows a process flow diagram of softening pretreatment process and abridged mass balance for a 300-gallon-perminute (gpm) system.

MVR AND STREAM-DRIVEN EVAPORATORS – Depending on the desired final wastestream, a "partial" ZLD system can be proposed—meaning that the system produces a final brine that may require further handling before disposal. Generally, a partial ZLD system consists of one or more evaporator systems producing a concentrated brine stream for disposal. Several types of evaporators exist and can be configured in multiple ways that reduce energy consumption including mechanical vapor recompression (MVR), as shown in Figure 5. A MVR falling film evaporator is most often selected as the primary evaporative technology. As needed, a secondary, steam-driven, forced circulation evaporator can be installed to remove additional distillate and further reduce the concentrated brine flow.



Figure 4: Softening Process Flow Diagram and Mass Balance

		Softening System							
P	arameter	FGD Settling Pond Effluent Thickener Overflow Softening Sludge Blowdown Softening Soli							Solids to Landfill
5	tream ID	1	1	1	2		3	4	
Flow	gpm	3	00	2	97	39			
-	MGD	0.	43	0.	43	<u>Ó</u> ,	06		
	cu ft/ day								1495
Density	g/mi	1	01	1.01		1.25			
Energy Para	meters					1			
pH		6	.6	10.4		10.4			
Temperature ("F)		*F) 77.0		79.8		79.8			
		Conc (mg/L)	Mass (lb/day)	Conc (mg/L)	Mass (lb/day)	Conc (mg/L)	Mass (lb/day)	Conc (mg/L)	Mass (lb/day)
Water			3578995		3539821		436686		39575
Total Disso	ved Solids	19421	19421 69839 22240 79440 7		22240	9800	1	888	
Total Suspe	nded Solids	23	81	30	109	9 168071 79163		79:	

Figure 5: MVR Evaporator Process Diagram



In an MVR evaporator, influent water to the evaporator is preheated using recovery heat exchangers (HEX) in contact with the hot distillate produced by the evaporator. The influent water is typically heated in two stages: the effluent water temperature of the first stage HEX is selected to optimize carbon dioxide gas stripping, and the effluent water temperature of the second stage HEX is selected at a temperature within near the boiling point. The compressor in an MVR evaporator achieves the remainder of the temperature rise necessary to vaporize the influent, but is limited in the boiling point rise it can accommodate. Figure 6 shows how incoming chloride and TDS concentrations can impact the boiling point rise and the water recovery efficiency.

Figure 6: Boiling Point Rise in an Evaporator versus Fraction Evaporated



A steam-driven, forced circulation evaporator is not directly limited by boiling point rise and can, therefore, be used to achieve brine concentration beyond that of an MVR evaporator. Similar to an MVR design, the forced circulation evaporator requires design considerations for heat exchangers based on the boiling point rise and recirculation. These evaporator systems, however, use a steam-duty brine heat exchanger to heat the feed stream and evaporator recirculation stream to the desired boiling point temperature.

In both evaporators, brine recirculation targets solids formation on the seed crystals (preferred solids) rather than the heat transfer surfaces, such as tube bundles. Recirculation from the underflow is used as seed material in the evaporator. Calcium sulfate is generally used as the preferred seeding material, due to its stability at the high evaporator temperature and pressure and its small particle form lending to larger surface area. Depending on the water chemistry, it is sometimes necessary to add calcium sulfate seed material if an insufficient amount is present to avoid scale formation and unfavorable solids compositions (e.g., large percentages of magnesium or silica solids).

Caustic is often added to these evaporator systems. Caustic demands and solids formation are limiting factors in determining the final brine flow and concentration. Caustic demands to maintain a neutral pH significantly increase as the brine flow rate is reduced and boiling point rise increases. The elevated temperature leads to increased dissociation of water and other thermally-dissociable compounds and to reduced solubility of magnesium hydroxide (Figure 7). Therefore, as the temperature increases, larger quantities of sodium hydroxide are consumed due to magnesium hydroxide precipitation. This causes a decline in pH and need for further sodium hydroxide addition. Magnesium hydroxide salts should be avoided, as these solids lead to scaling issues. If a model shows formation of magnesium hydroxide solids, the evaporator pH can be lowered to the point that magnesium hydroxide solids no longer form. However, lowering the pH leads to increased risk for corrosion, requiring evaluation of the system viability.



Figure 7: Caustic Requirements versus Magnesium Hydroxide Solids Formation

Note: This simulation was run at 15,000 mg/L Cl-, 25,500 mg/L TDS, and 0.08 fraction of final/initial concentration.

Table 2 summarizes models of a forced circulation evaporator at different recoveries and caustic additions. The table shows how these targets impact the boiling point and final total suspended solids (TSS) concentration in the brine.

Brine Flow			Boiling	TSS in
(Fraction	Caustic		Point	Brine
of Original	Addition	рН	Temp.	(%
Flow)	(gpm)	(s.u.)	(°F)	mass)
0.1	0.2	6.22	227.9	0.09%
0.075	0.2	5.7	237.68	0.13%
0.075	0.4	5.89	237.6	0.35%
0.05	0	3.63	261.97	0.20%
0.05	0.2	4.99	260.65	0.95%

Table 2: Brine Concentration Evaluation for Forced Circulation Evaporator

When treating unsoftened wastewater, TSS in the brine stream should consist primarily of calcium sulfate. Other solids typically observed in the evaporator are calcium fluoride, magnesium fluoride, silicon dioxide, and barium sulfate. Concentrated brine can contain extremely high concentrations of chloride and suspended solids. Therefore, storage tanks, pumps, and piping must be designed to accommodate the corrosive, abrasive, and plugging nature of the concentrated brine slurry. Tanks must have agitators and piping designed to maintain adequate velocity to prevent plugging. Lines either must be flushed when shut down, or kept in circulation using recirculation loops. As salts can precipitate out or cement up on cooling, it may be necessary to keep brine storage tanks and pipes heated and insulated. One option to avoid this is to dewater the brine to remove the solids, but this, in turn, can cause issues to secondary evaporative processes that require seed material. Alternatively, the solids can be retained in the brine and mixed with materials, such as fly ash, to be disposed in a landfill.

FORCED CIRCULATION CRYSTALLIZER – A forced circulation crystallizer is the more conventional crystallization process. A general process diagram is shown in Figure 8. This process operates similar to the forced circulation evaporator, though it typically operates at a significantly higher temperature. For this type of crystallizer, the water chemistry must be reviewed to determine whether it can be used.





Calcium and magnesium salts are difficult to crystallize at atmospheric pressure, because the solubility increases as the temperature rises, resulting in extremely high salinities and boiling point before crystallization occurs. Also, the crystallizer has similar problems with caustic usage and magnesium hydroxide formation in evaporator systems. Therefore, depending on the incoming water chemistry, it is typically necessary to implement a pretreatment softening step first, to reduce water hardness and replace calcium and magnesium with sodium. Sodium chloride can be crystallized at a much lower boiling point than calcium and magnesium chloride salts.

Crystallizers represent "full" ZLD systems rather than partial ZLD systems, in that the final concentrate is removed as a salt cake and landfilled. The salts present in the stream dictate the moisture content and density that can be reached in the final salt cake.

VACUUM FORCED CIRCULATION CRYSTALLIZER -

The main advantage of a vacuum, lowtemperature, forced circulation crystallizer is the use of an applied vacuum to lower the boiling point of the brine—in some cases eliminating the need for preheating the brine (Figure 9).

Figure 9: Vacuum, Forced Circulation Crystallizer **Process Diagram**

 \rightarrow Salt

(CaCl₂, MgCl₂)

Compressor

Pump

Hot

Distillate

Similar to the previous crystallizer, water chemistry is the most important design consideration. As mentioned previously, calcium and magnesium salts pose problems in conventional crystallization, but it is possible to crystallize these salts at low pressures. Other highly soluble salts that may pose crystallization problems include chlorides, nitrates, and salts of organic acids. Calcium chloride and magnesium chloride solids are most commonly formed. The major advantage of using this crystallizer technology is that the process does not require softening pretreatment to remove these components. When modeling or evaluating this technology, it still important to consider solubility and composition of salts.

One additional concern of the final salt cake is that calcium chloride and magnesium chloride are hygroscopic, meaning that in humid areas, Vacuum. they have a tendency to absorb moisture from air. This must be considered when evaluating disposal options.

Table 3 compares the operational requirements for MVR evaporation, forced cil culation crystallization, and vacuum forced cr /stallization systems.



MVR	Forced Circulation	Vacuum	

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	Evaporation	Crystallization	Crystallization
Polymer (gpd)	-	1	-
Hydrated Lime (lb/d)	-	11,000	-
Sodium Carbonate (lb/d)	-	55,000	-
Sulfuric acid (gpd)	10	300	10
Antiscalant (gpd)	4	4	4
Antifoam (gpd)	4	4	4
Sodium Hydroxide (gpd)	450	150	450
Solids generation (cu ft/d)	100	1,900	1,000
Labor (FTEs)	7	10	9
Power Load (MW)	2.3	2.4	2.5
Cooling Water (gpm)	90	800	700
Steam (1,000 lb/hr)	0	20	0

CONCLUSIONS

The chemistry of FGD blowdown or other wastewaters must be carefully evaluated when considering ZLD treatment technologies. Commercial software such as StreamAnalyzer™, Aspen™, and Aspen OLI™ can model the complex water chemistry observed in these ZLD applications. The chemical composition especially chlorides, calcium, and magnesium will drive pretreatment requirements and viable technologies. Disposal methods also should be evaluated to take advantage of disposal options for landfilling concentrated brines with fly ash and gypsum, so long as the supply and commercial demand are favorable.

REFERENCES

Environmental Protection Agency (2009). Steam Electric Power Generating Point Source Category: Final Detailed Study Report. *EPA 821-R-09-008*.