Zero Liquid Discharge Effluent Guidelines Compliance Strategies for Coal-Fired Power Plants' FGD Wastewater

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ABSTRACT

The U.S. Environmental Protection Agency's (EPA) proposed Effluent Guidelines for the Steam Electric Power Generating Category was published in June 2013. The proposed Effluent Guidelines provide new discharge limitations on various metal species in certain waste streams (i.e., mercury, arsenic, selenium) and nitrates/nitrites. The most significant impact of the proposed changes will be to coal-fired power plants that discharge flue gas desulfurization (FGD) wastewater and fly ash or bottom ash transportation water. Once the rule is finalized, the new limits will be incorporated into National Pollutant Discharge Elimination System (NPDES) permits as the permits enter renewal cycles.

Coal-fired power plants with newer wet FGD applications more commonly include physical/chemical wastewater treatment facilities, which remove mercury and arsenic through precipitation and filtration. In order to be in compliance with the proposed Effluent Guidelines, these stations will likely require further treatment to remove remaining nitrates/nitrites and selenium via biological treatment or eliminate the waste stream altogether (zero liquid discharge or ZLD).

Using a case study, this paper evaluated different combinations of ZLD approaches, such as a brine crystallizer/evaporator, a wastewater spray dryer and fixation/stabilization, to achieve compliance with the proposed Effluent Guidelines for coal-fired power plants with existing physical/chemical wastewater treatment facilities on their wet FGDs. In order to reduce the cost of ZLD approaches, variation of plant operation with changes in FGD absorber material of construction and the variations in capital and operating costs impacts will be presented, as part of this evaluation.

KEYWORDS:

Flue gas desulfurization, wastewater, zero liquid discharge, gypsum, sulfur dioxide, equilibrium chlorides, blowdown, brine crystallizer/evaporator, wastewater spray dryer, fixation, stabilization.

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1.0 Introduction

Coal-fired power plants that discharge flue gas desulfurization (FGD) wastewater will be significantly impacted by the proposed Effluent Guidelines for the Steam Electric Power Generating Category published by the U.S. Environmental Protection Agency (EPA) in June 2013. The proposed Effluent Guidelines will enforce new discharge limitations on various metal species in certain waste streams (i.e., mercury, arsenic, selenium) and nitrates/nitrites. There are a number of treatment technologies available for the reduction of metal species' concentrations including, but not limited to, physical/chemical treatment, biological treatment, and thermal evaporative or zero liquid discharge (ZLD) systems. Coal-fired power plants with newer wet FGD applications usually include existing physical/chemical wastewater treatment facilities, which remove mercury and arsenic through precipitation and filtration. In order to be in compliance with the Effluent Guidelines, these stations will likely require further treatment to remove remaining nitrates/nitrites and selenium via biological treatment or a ZLD approach.

To achieve compliance with the proposed Effluent Guidelines for coal-fired power plant with existing physical/chemical wastewater treatment on their wet FGDs, this case study will evaluate different combinations of ZLD approaches, including a brine crystallizer/evaporator, a wastewater spray dryer and fixation/stabilization, for FGD wastewater treatment only (this case study does not consider any other wastewater sources). The cost of a ZLD system to meet the proposed Effluent Guidelines discharge limits will be based on the flow rate processed by the ZLD system. To reduce the cost of the ZLD approaches, modifications to plant operation through changes in FGD absorber (and other related process equipment) materials of construction will be evaluated. An optimum combination of FGD absorber materials costs and ZLD system costs will be evaluated to identify the minimum cost combination for compliance with the proposed Effluent Guidelines.

2.0 Case Study Unit Assumptions

For the purpose of this paper, a 500 MW coal-fired unit that fires bituminous coal (approximately 2.4% sulfur) is assumed to be equipped with a forced oxidation, wet limestone FGD to remove sulfur dioxide (SO_2) from the flue gas through means of contact with limestone slurry scrubbing liquor. The FGD system on this unit is assumed to collect approximately 97% of the SO_2 and a similar percentage of the hydrogen chloride (HCl) in the flue gas. The SO_2 chemically reacts with the slurry and forms mainly calcium sulfate ($CaSO_4 \cdot 2H_2O$), also known as gypsum, which is a main component of wallboard gypsum.

The chloride becomes a dissolved solid and the chloride concentration continually increases until equilibrium is reached in the FGD system's closed slurry loop. As this chloride concentration continues to increase, the slurry becomes more and more corrosive to the metallic materials of construction of the absorber. The FGD system requires a chloride purge stream to be discharged from the FGD absorber, via the gypsum dewatering system, a two stage hydroclone system, to control chloride levels to below the absorber material's corrosion limits. For this case study, it is assumed that the scrubber vessel was initially designed for 8,000 ppm chlorides and, based on the operating chloride equilibrium level, constructed with Stainless Steel, 317 LMN (S317226).

The wastewater will have high concentrations of heavy metals, chloride, biochemical oxygen demand (BOD), phosphate, total suspended solids (TSS) and nitrogen. The scrubber blowdown stream is treated in a dedicated FGD wastewater treatment (WWT) facility, which consists of a chemical/physical treatment system. The treatment facility is assumed to have been designed to meet the current effluent limits for mercury (0.242 µg/L daily maximum and 0.119 µg/L thirty (30) day monthly average) and arsenic (8 µg/L daily maximum and 6 µg/L thirty (30) day monthly average). The WWT system reduces total suspended solids, adjusts the pH, desupersaturates the stream, and reduces heavy metals.

It is assumed that the FGD detwatering system was originally designed to be capable of producing wallboard grade gypsum, which would require a chloride level in the wallboard of approximately 100 ppm. However, it is assumed that the unit does not currently produce wallboard grade gypsum and only produces gypsum with a 90-wt% solids content to be disposed of in a landfill with a higher chloride concentration.

Based on the assumptions listed above, a hypothetical FGD tower was sized, and the resulting parameters are shown in Table 2-1.

Table 2-1: FGD Tower Sizing Based on Assumptions

Parameter	**Units**	**Value**
Absorber Tower Diameter	ft	65
Absorber Tower Height	ft	150
Absorber Tower Surface Area	ft^2	34,000
Design Chloride Equilibrium	ppm	8,000
Absorber Tower Original Material of Construction		S317226
Blowdown Rate	gpm	81
Inlet Duct Dimensions, Length x Width	ft	30 x 30
Outlet Duct Diameter	ft	30
Inlet Duct Original Material of Construction	ft	CS
Outlet Duct Original Material of Construction	ft	C-276

3.0 Zero Liquid Discharge Options

In order to be in compliance with the Effluent Guidelines, different options of thermal evaporative or zero liquid discharge (ZLD) systems for the case study are discussed further in the following sections.

3.1 Brine Crystallizer/Evaporator

The brine crystallizer/evaporator ZLD approach utilizes heat from a steam source to evaporate liquid to concentrate salts for dewatering and disposal. This leaves a solid material that must either be stored on site or transported by truck to a landfill off site. A brine crystallizer/evaporator will produce a high purity water stream that can be reused elsewhere in the station. It should be noted, however, that this case study does not account for reuse of water as boiler makeup, cooling tower makeup, or other environmental control processes.

3.2 Wastewater Spray Dryer

A wastewater spray dryer ZLD approach transfers FGD blowdown to a spray dryer vessel in which hot flue gas, prior to the air preheater, is diverted from the main flue gas path to evaporate the liquid. The FGD blowdown is taken from the overflow of the secondary hydroclone, no longer requiring the use of the existing physical/chemical WWT facility. The outlet of the wastewater spray dryer reconnects to the flue gas path before a particulate collection device, i.e. electrostatic precipitator (ESP) or baghouse, so that the waste solids can be collected in the downstream equipment. If a station sells its fly ash, this ZLD approach may have an impact on fly ash quality that would need to be evaluated.

3.3 Fixation/Stabilization

Wet FGD waste or gypsum can be stabilized by mixing a weight proportioned blend of FGD blowdown, gypsum, fly ash and quicklime for disposal in a landfill. This reaction uses the station’s fly ash as a cementing agent. This approach reduces the ability to sell fly ash used for commercial products and requires extra landfill volume. The basic pozzolanic reaction is an acid-base reaction between lime and silicic acid (H_4SiO_2).

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \rightarrow CaH_2SiO_4 \cdot 2H_2O \qquad [1]$$

The resulting fixated waste is physically stable making it easy to handle via belt conveyor and/or dump truck. The mechanism for this display of strength is the reaction of silicates with lime to form secondary cementitious phases (calcium silicate hydrates with a lower Ca/Si ratio) which display gradual strengthening properties usually after seven (7) days. The fixated waste is incompletely saturated, because of the chemical reactions which occur, develops an increasingly lower permeability with the result that saturation would take years, if ever, to occur. This approach to fixating waste is useful for landfill disposal due to forming a near-impermeable mass which resists reliquification, channeling and minimizing leaching to ground or surface waters.

Requirements for the proportions of the fixated blend should be tested prior to the design of the associated equipment.

3.4 ZLD System Sizing & Costs

A decisive factor in the cost of a ZLD system to meet the proposed Effluent Guidelines will be the flow rate processed by the ZLD system. Typically, a newly installed ZLD system would be used to treat all plant wastewater. However, it should be noted that this study will only consider ZLD systems sized exclusively for the FGD blowdown stream. Using the same base design assumptions listed in Table 2-1 and Sargent & Lundy, L.L.C. (S&L) in-house cost data, the net present value costs of the three ZLD options evaluated for a twenty (20) year period at a 7.04% discount rate are summarized in Table 3-1 below, in constant 2014 dollars.

Table 3-1: ZLD System Costs

ZLD System	**Brine Crystallizer/ Evaporator**	**Wastewater Spray Dryer**	**Fixation Stabilization**
Equilibrium Chlorides (ppm)	8,000	8,000	8,000
Design Blowdown (gpm)	81	81	81
Installed Capital Cost	**$36.8M**	**$25.0M**	**$17.0M**
O&M	**$3.7M**	**$1.8M**	**$1.6M**
Net Present Value (NPV)	**$88.9M**	**$51.9M**	**$40.2M**

The O&M costs listed in Table 3-1 include variable O&M costs for auxiliary power, reagents/chemicals, and waste disposal and also includes fixed O&M costs for operating labor and maintenance labor and materials.

4.0 ZLD System Cost Optimization

To reduce the cost of ZLD approaches, the purge stream can be reduced by changing the absorber material of construction. The base case assumes that each of the ZLD systems are sized exclusively for the FGD blowdown stream, as listed in Table 2-1. To estimate the costs, various alternate materials were compared to estimate the associated reduction in the FGD purge rate, ZLD capital and O&M cost, and the overall cost of the smaller ZLD systems plus the new absorber linings were compared to the base case costs show in Table 3-1.

4.1 Equilibrium Chloride Impacts

As mentioned previously, as the chloride concentration increases in the FGD system's slurry loop, the slurry becomes more and more corrosive to the metallic materials of construction of the absorber. Eventually, a high chloride concentration will also have a detrimental effect on the performance of the FGD system. To control chloride concentrations to within the material's limitations, the blowdown stream purges chlorides from the system.

To reduce the amount of purged FGD blowdown, the equilibrium chloride concentration in the absorber vessel will need to be increased. The original material of the absorber vessel, S317226, limits the equilibrium chloride content to 8,000 ppm, and can withstand an excursion chloride concentration of 15,000 ppm. However, the safe level of operation is not at the maximum chloride concentration, but at the level of "design chlorides." Therefore, the absorber vessel will need to be modified to be able to withstand higher chloride concentrations.

4.2 FGD Absorber Modification Options based on Equilibrium Chlorides

This study does not consider chloride concentrations greater than 50,000 ppm. When chloride concentrations are greater than 50,000 ppm, the chloride will react with the soluble calcium to form calcium chloride ($CaCl_2$). At elevated concentrations of chloride, the soluble $CaCl_2$ begins to block dissolution of calcium into the slurry. If this occurs, the pH could drop and the SO_2 removal capability of the FGD system would be diminished. Alkalinity can be increased by increasing the flow of limestone slurry into the system by increasing the liquid-to-gas ratio (L/G) or through the use of additives such as sodium, magnesium, or organic acids (dibasic, adipic). These additives, in effect, tie-up the chlorides and allow for the available alkalinity to react with the SO_2 in the flue gas. With a chloride concentration above 50,000 ppm, these additives are almost mandatory to avoid a large increase in the system limestone usage.

Table 4-1 lists the absorber modification options to reduce blowdown quantities and the associated equilibrium chloride level concentration. For the purpose of this paper, the three options, vinyl ester lining, C-276 wallpaper, and ceramic tile lining, were chosen to be evaluated due to each of their proven performance in the power industry, low maintenance, long service life, and ability to be applied numerous types of FGD absorber original materials of construction. It should be noted, however, that the three options do not all have the same life expectancy, maintenance, or costs. The costs of the three options are shown in Table 4-3, but the detailed comparison of the options is beyond the scope of this discussion.

Table 4-1: Equilibrium Chloride Levels of Modification Options[1]

Absorber Modification Options	Design Equilibrium Cl^- (ppm)	Excursion Cl^- (ppm)[2]	Blowdown Rate (gpm)
Vinyl Ester Lining	50,000	100,000	13
C-276 Wallpaper	50,000	100,000+	13
Acid Resistant, Ceramic Tile Lining	50,000	100,000+	13

1. Calculations based on case study assumptions listed in Section 2.
2. Equilibrium chloride level is a very design-specific variable. These values are examples of chloride levels, but in no way are indicative of all systems.

When operating above 20,000 ppm of chlorides, additional slurry capacity is also needed to increase the L/G ratio. The additive usage and additional slurry capacity will add additional capital and operating and maintenance (O&M) costs. This will alleviate any problems with higher chloride levels inhibiting the scrubbing of incoming flue gas. The additional cost is detailed further in Table 4-5.

In order to avoid any additional costs related to operation above 20,000 ppm of chlorides, an additional sensitivity analysis is evaluated for this case study at a limited equilibrium chloride concentration. Limiting the chloride concentration to 20,000 ppm will require the ZLD system to treat a larger amount of blowdown, which will result in a higher capital cost ZLD system. The blowdown rate associated with limiting the equilibrium chloride concentration is listed in Table 4-2.

Table 4-2: Limited Equilibrium Chloride Levels of Modification Options[1]

Absorber Modification Options	Limited Equilibrium Cl^- (ppm)[2]	Blowdown Rate (gpm)
Vinyl Ester Lining	20,000	32
C-276 Wallpaper	20,000	32
Acid Resistant, Ceramic Tile Lining	20,000	32

1. Calculations based on case study assumptions listed in Section 2.
2. Equilibrium chloride level is a very design-specific variable. These values are examples of chloride levels, but in no way are indicative of all systems.
3. Limited design maintains chloride concentration below 20,000 ppm to avoid additional costs associated with operation at higher chloride concentrations.

4.3 System Cost Optimization

Using in-house cost data, S&L sized each of the ZLD options exclusively for the FGD blowdown stream at the volumetric flow rates resulting from limiting the equilibrium chloride concentration. The following Table 4-4 and Table 4-5 show the total installed costs for the absorber modification options to increase the design chloride level. From this, the costs of the absorber liner modifications can be calculated and added to the reduced costs of the ZLD systems to determine a low-cost solution. It is assumed that the liner options would not require replacement during the twenty (20) year evaluation period. O&M costs for regular maintenance of all the liners are included in the evaluation and in order to be conservative, assumed to be \$100,000 per year. Table 4-4 and Table 4-5 also summarize the net present value costs of the new absorber liner and the resized ZLD system evaluated for a twenty (20) year period at a 7.04% discount rate, in constant 2014 dollars. The costs presented do not include cost of lost generation of revenue during the absorber lining installation (assumed to be similar for all options), owner's costs, or allowance for funds using during construction (AFUDC).

Table 4-3: Modification Option Materials Unit Pricing

Absorber Modification Options	Material Cost (\$/ft^2)	Installation Cost (\$/ft^2)[1]	Final Installed Cost (\$/ft^2)
Vinyl Ester Lining	28	66	94
C-276 Wallpaper	41	58	99
Acid Resistant, Ceramic Tile Lining	48	58	106

1. Installation costs include scaffolding to remove the old liner and install the new liner, and assume that the work will be done in two-shifts in order to complete the lining during an already scheduled, four-week outage.

It should be noted that the selection of the absorber liner modification for an actual project would be evaluated in detail based on plant-specific design requirements.

Table 4-4: Low-Cost Solution Analysis – 20,000 ppm Equilibrium Chlorides

ZLD System	**Brine Crystallizer/ Evaporator**			**Wastewater Spray Dryer**			**Fixation Stabilization**		
Base ZLD Cost									
Equilibrium Cl$^-$ (ppm)	8,000			8,000			8,000		
Design Blowdown (gpm)	81			81			81		
ZLD Installed Cost	$36.8M			$25.0M			$17.0M		
ZLD O&M	$3.7M/yr			$1.8M/yr			$1.6M/yr		
Costs for Reduced Blowdown									
New Absorber Liner	**Vinyl Ester**	**C-276**	**Tile**	**Vinyl Ester**	**C-276**	**Tile**	**Vinyl Ester**	**C-276**	**Tile**
Equilibrium Cl$^-$ (ppm)	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000
Design Blowdown (gpm)	32	32	32	32	32	32	32	32	32
Liner Installed Cost	$3.2M	$3.4M	$3.6M	$3.2M	$3.4M	$3.6M	$3.2M	$3.4M	$3.6M
Liner O&M	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr
Reduced ZLD Installed Cost	$21.1M			$14.3M			$9.8M		
Reduced ZLD O&M	$2.3M/yr			$1.3M/yr			$1.4M/yr		
NPV	**$58.4M**	**$58.6M**	**$58.9M**	**$38.4M**	**$38.6M**	**$40.0M**	**$33.6M**	**$33.8M**	**$34.1M**

Table 4-5: Low-Cost Solution Analysis – 50,000 ppm Equilibrium Chlorides

ZLD System	**Brine Crystallizer/ Evaporator**			**Wastewater Spray Dryer**			**Fixation Stabilization**		
Base ZLD Cost									
Equilibrium Cl^- (ppm)	8,000			8,000			8,000		
Design Blowdown (gpm)	81			81			81		
ZLD Installed Cost	$36.8M			$25.0M			$17.0M		
ZLD O&M	$3.7M/yr			$1.8M/yr			$1.6M/yr		
Costs for Reduced Blowdown									
New Absorber Liner	**Vinyl Ester**	**C-276**	**Tile**	**Vinyl Ester**	**C-276**	**Tile**	**Vinyl Ester**	**C-276**	**Tile**
Equilibrium Cl^- (ppm)	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000
Design Blowdown (gpm)	13	13	13	13	13	13	13	13	13
Liner Installed Cost	$3.2M	$3.4M	$3.6M	$3.2M	$3.4M	$3.6M	$3.2M	$3.4M	$3.6M
Liner O&M	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr	$0.1M/yr
Additional Costs for High Chloride Concentration									
High Cl^- Equipment Upgrade Cost	$2.8M			$2.8M			$2.8M		
High Cl^- Equipment Upgrade O&M	$0.4M/yr			$0.4M/yr			$0.4M/yr		
Reduced ZLD Installed Cost	$12.3M			$8.3M			$5.7M		
Reduced ZLD O&M	$1.7M/yr			$1.1M/yr			$0.4M/yr		
NPV	**$48.4M**	**$48.7M**	**$49.0M**	**$36.5M**	**$36.7M**	**$37.0M**	**$24.7M**	**$24.9M**	**$25.2M**

4.4 Other Balance of Plant Considerations

Power plants usually have a long term coal contract, therefore, it should be noted that change in operation to firing coal with a higher sulfur to chloride (S:Cl) ratio would result in several changes. The most significant to note is that the amount of blowdown varies inversely with the change in S:Cl ratio, in that if the S:Cl ratio decreases, the blowdown rate will increase. Therefore, major changes in coal sources should consider the impact to the capacity of the installed ZLD system.

The modifications to the absorber vessel will increase the equilibrium chloride concentration in the absorber vessel and the FGD blowdown stream. As the FGD blowdown stream would be more corrosive with a higher chloride concentration, materials of all downstream equipment including, piping, hydroclones, pumps, etc. that handle the FGD blowdown should be evaluated to determine if other equipment needs to be replaced or modified in order to also handle the higher chloride concentration.

As a result of the implementation of the proposed Effluent Guidelines and ZLD approach, station permits, such as National Pollutant Discharge Elimination System (NPDES) permits and point source air emissions permits, will need to be modified. As part of the permitting effort, additional in-plant and effluent monitoring may be required. Considerations should be made for possible landfill leachate treatment, as required.

Two of the ZLD systems, the brine crystallizer/evaporator and the wastewater spray dryer will have significant impacts on the heat rate of the units. Costs of heat rate impacts have not been included as part of this paper. Therefore, should one of these two ZLD systems be used for a ZLD approach for compliance, a detailed study of heat rate impacts and the resulting costs should be included in case-by-case analysis.

5.0 Summary and Recommendations

Any ZLD system would be highly plant-specific, and the results above represent a hypothetical unit constructing a new ZLD wastewater treatment system specifically for the FGD blowdown and relining the existing absorber vessel. Typically, a ZLD system would treat all wastewater from the plant. However, this is beyond the scope of this discussion. As indicated in Table 4-4 and Table 4-5, the reduction of the FGD blowdown flow rate by operating at 20,000 ppm or 50,000 ppm chloride rather than the base 8,000 ppm level significantly reduces the cost of the ZLD systems, and the lowest net present value ZLD system for both chloride concentrations would be to install a fixation stabilization system and reline the absorber with a vinyl ester liner. The reduction in the overall ZLD system cost would offset the cost of the absorber liner modifications. As mentioned previously, outage costs are not included for the relining of the vessel, as it was assumed that the lining work would be completed during an already planned outage. It should be noted that if the duration of the lining work extended the outage, the costs would be significantly impacted.

As is the case with most decisions regarding emission control from a utility power plant, the decisions to be made are plant-specific. A case-by-case analysis, similar to this, must be performed before making any decisions regarding potential ZLD approaches and absorber modifications for compliance with the proposed Effluent Guidelines.

6.0 References

1. Katzberger, Steve; and Sloat, David; *Evolution FGD Materials of Construction Selection and Optimization of FGD and Wastewater Treatment System Design*, October 2008.
2. Federal Register Notice, pre-publication (PDF) (491 pp, 1.2MB) April 19, 2013 (http://water.epa.gov/scitech/wastetech/guide/steam-electric/upload/steam_prepub.pdf