

Considerations Impacting the Technology Selection Process for FGD Purge Stream Wastewater Treatment Systems

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Abstract: With the more stringent air emissions standards that are being legislated in the US, both new and existing coal-fired power plants are installing flue gas desulfurization (FGD) systems. While reducing air-borne pollutants released from the plant, these systems create a wastewater stream that is challenging to handle because of its metals, organics, high chlorides, and high suspended solids content. As a result of the increased regulatory attention given to this waste stream and the complex treatment schemes associated with meeting the ever-tightening plant water discharge permit limits, this wastewater is a growing concern for many plant operators and designers. The targeted constituents that typically need to be addressed for treatment in FGD wastewater include heavy metals such as mercury, selenium, and arsenic as well as any organic compounds that are added to the FGD absorber to enhance SO₂ removal. Due to the high dissolved solids content of this wastewater stream, recycling this stream for reuse internally in the power plant, even after treatment for removal of metals and suspended solids has been performed, is normally quite difficult. Frequently the only options available for the ultimate disposal of this wastewater are discharge under regulatory purview and predicated conditions or crystallization in a zero liquid discharge system. This technical paper will examine the various treatments and reuse options available and discuss the issues influencing the design choices. Several case histories where FGD wastewater treatment systems have been designed for discharge of FGD wastewater and/or zero liquid discharge systems employed will be detailed.

INTRODUCTION

Flue gas desulfurization (FGD) systems are necessary components of today's generation of coal-fired power generating facilities. The predominant rationale for the inclusion of this equipment is normally control of SO₂ emissions in the flue gases. However, as air emissions standards continue to become more stringent, FGD equipment suppliers and system designers also continue to find methods to improve the efficiency of these systems in not only removing SO₂, but also reducing the concentrations of heavy metals and other contaminants from the flue gas stream. While cleaning up the flue gases that are emitted via power plant stacks, wet FGD systems produce a purge wastewater stream containing these heavy metals and high levels of suspended solids.

As environmental water discharge regulations and National Pollutant Discharge Elimination System (NPDES) permits continue to get tougher with

respect to the quality and quantity of wastewaters that can be released from power plant facilities, the options for treatment and ultimate disposal of the FGD purge stream grow in complexity as well as expense. On many of the coal-fired power projects undergoing conceptual design and permitting today, how to handle, treat, and dispose of this waste stream has become a major concern requiring design commitments early in the project development process.

While many studies have been conducted to determine the most practical and simplified licensing and design approach for permitting and constructing treatment and disposal facilities for FGD wastewater, the numerous variables that need to be considered for each specific plant site make standardization of the FGD wastewater treatment system nearly impossible. Site specific issues such as the type of fuel burned, quality of FGD reagents used, the requirements of potential water discharge locations,

the availability of sludge disposal sites, and the design criteria of the wet FGD absorber system factor into the decision making processes for permitting and designing each individual treatment and disposal facility.

TREATMENT OPTIONS

Physical/Chemical Precipitation Processes

Currently the most widely utilized methods for treating wet FGD purge streams are physical/chemical precipitation processes. The technologies used in FGD wastewater treatment include hydroxide, carbonate, and sulfide precipitation processes utilizing coagulation and metal co-precipitation processes. Metal effluent concentrations achieved by these various processes vary depending on the solubility of metal species that are targeted for precipitation. Lowest concentrations, however, are typically achieved by precipitating metals in the sulfide form. For instance, consider the precipitation of dissolved mercury. In precipitation of mercury as a metal hydroxide or as a metal sulfide, the solubility product of mercury (II) hydroxide $\text{Hg}(\text{OH})_2$ is 3.2×10^{-26} while the solubility product of mercuric sulfide Hg_2S is 1.0×10^{-47} ⁽¹⁾.

The physical/chemical precipitation processes, when utilized as the primary wet FGD wastewater treatment system, are commonly combined into two process schemes: hydroxide/carbonate precipitation and hydroxide/sulfide precipitation. Both process schemes also commonly employ coagulation/co-precipitation principles where a coagulant such as alum or ferric chloride is added to the wastewater stream to improve contaminant reduction through adsorption of the contaminants onto the bulk sludge produced.

Two clarification steps are typically employed in both process schemes with primary suspended solids reduction and hydroxide precipitation in the first clarification step through pH adjustment and sulfide or carbonate precipitation occurring in the second clarification step. This sequence optimizes chemical consumption and reduces the utilization of expensive reagents, particularly sulfide reagents such as proprietary organosulfide products. Final media filtration commonly follows these precipitation sequences to ensure removal of fine suspended particles that may still contain oxides of metals.

Biological Treatment

Aerobic and anaerobic biological treatment processes are generally utilized in a wet FGD wastewater treatment system for the reduction of biological oxygen demand (BOD), generated by the reduction of organics, and heavy metals present in the FGD wastewater. Selenium is currently the most commonly targeted heavy metal when designing biological treatment systems for treating this wastewater stream. The biological processes are typically preceded by physical/chemical treatment for reduction of suspended solids and more effective utilization of the microorganisms controlling the biological process. The physical/chemical treatment equipment is then followed by either aerobic or anaerobic treatment components or both depending on the compounds targeted for removal and reduction. Aerobic bacteria are utilized to remove organics, particularly in the form of BOD, from the wet FGD purge wastewater. The most common source of BOD in wet FGD purge wastewater is from the addition of dibasic acid (DBA) or other organic products in the FGD absorber vessel to optimize scrubber performance. Anaerobic bacteria such as sulfate reducing bacteria (SRB) can be utilized to remove selenium from the wet FGD purge stream. Selenium may be present in the form of selenates, selenites, or elemental selenium in the wet FGD purge wastewater. The anaerobic bacteria utilize the oxygen present in the selenate forms and in the sulfates present in the wastewater stream for respiration and, in the process, reduce the selenates to elemental selenium which can be removed from the wastewater by means of clarification processes.

Constructed Wetlands

Constructed wetlands treatment systems (CWTS) are designed to utilize microorganisms and plants such as bulrush and cattails to remove pollutants from the wet FGD purge wastewater. A typical CWTS treatment train includes a settling basin or clarifier as a pretreatment step to remove suspended solids. The clarifier is followed by a series of wetland cells and aeration cells. The wetland cells are designed to accomplish targeted metals reduction. For instance, bulrush cells are typically utilized to target mercury and selenium removal from the wastewater stream ⁽²⁾. The aeration cells, commonly consisting of rock filters, add dissolved oxygen to the wastewater stream to promote oxidization of iron species in the wastewater to ferric oxides and ferric hydroxides ⁽²⁾. The oxidized iron species help with the removal of

heavy metals such as selenium and mercury from the wastewater through co-precipitation processes.

CWTS offer an option for treatment of wet FGD purge wastewater that is natural and environmentally friendly. However, they do require that the power plant have available a significant acreage of land for installation of the system. The wet FGD purge wastewater may also need to be diluted with water from a low total dissolved solids (TDS) source prior to treatment in the CWTS as high chloride concentrations, which are typical of this wastewater stream, may be toxic to some plants and associated wildlife.

PERMITTING AND LICENSING APPROACHES

Permitted Outfall or Discharge

The most typical licensing approach for disposal of wet FGD wastewater is discharge via a permitted outfall from the plant as an individual outfall or as a combined outfall with other wastewater streams from the power generating facility. While still one of the most common and usually the first attempted licensing approach, this scenario is not appropriate or feasible for every power plant facility. Case Study #1 presents a review of a coal-fired power generating facility retrofit project where this licensing approach was employed. A treatment system was designed to reduce the suspended solids and heavy metals concentrations in the wet FGD purge wastewater to allow it to be discharged via a combined outfall under the regulation of the plant's NPDES permit.

Where mixing zone provisions exist and are able to be permitted for once-through cooling water systems, the FGD wastewater stream may be able to be mixed with the condenser cooling water prior to discharge via the plant outfall. This licensing approach can significantly reduce the impact of very stringent metals discharge limits on the design of the FGD wastewater treatment system. Case Study #5 presents a case where this approach was utilized for the design of a new coal-fired power generating facility.

Internal Recycle of Treated/Untreated Wastewater

Recycle of the treated or untreated wet FGD purge stream is one of the first licensing and design approaches analyzed regardless of whether or not the facility is able to obtain a discharge permit for the wastewater stream. Common applications suitable for reutilization of this wastewater stream include

dust suppression, flyash or by-product stabilization, and bottom ash transport. Case Study #2 presents a case where treatment of the wet FGD wastewater stream was optimized for a new coal-fired power plant to allow for recycle of the entire wastewater stream for by-product stabilization purposes. The plant, in this case, is not able to discharge this stream with other plant wastewater streams under its NPDES permit.

Another potential reuse application for treated wet FGD purge wastewater is as makeup to the plant equipment cooling water system (i.e. as cooling tower makeup). The contribution of chlorides and trace heavy metals by the treated wet FGD wastewater is incorporated into the cooling tower circulating water and drift calculations to analyze the potential impact on materials of construction as well as any environmental impacts due to cooling tower drift TDS or National Ambient Air Quality Standards (NAAQS) PM₁₀ regulations. The wastewater characterization and plant water balance detailing this scenario must be included with the application for permit to confirm the acceptability of this licensing scenario. Case Study #3 presents a case in which this scenario was developed as part of a licensing application for a new coal-fired power generating facility.

Deep Well Injection

Deep well injection of treated wet FGD purge wastewater is a licensing scenario that has been rapidly gaining popularity in recent years. This scenario involves treating the wastewater stream for reduction of total suspended solids (TSS) and sometimes scaling compounds prior to injecting it into wells thousands of feet below the earth's surface. Standard criteria for most deep well injection facilities require as a minimum that the wastewater to be injected have a TSS less than 100 mg/l and be filterable through a 5 micron filter. For wet FGD purge wastewater, this design and licensing approach generally requires pretreatment of the wastewater stream in a clarifier for suspended solids reduction followed by two stages of filtration, i.e. roughing media filter followed by fine filtration through a 5 micron cartridge filter. The cartridges are replaced with new cartridges when expended in lieu of backwash to avoid dealing with an additional FGD wastewater stream.

Zero Liquid Discharge

Zero liquid discharge (ZLD) is generally the last option analyzed for ultimate disposal of this

wastewater stream. This design and licensing approach normally includes pretreatment of the wastewater stream in a clarifier/cold lime softener for suspended solids and hardness reduction followed by concentration in a brine concentrator/evaporator and a crystallizer. Since the wet FGD purge stream is high in both calcium and magnesium as well as chlorides (see Table 1 for a typical wet FGD purge wastewater stream chemistry), the calcium chloride and magnesium chloride salts present in this wastewater stream could result in a very high scaling potential within the ZLD concentrator vessels. The pretreatment step reduces the scaling potential in the downstream brine concentrator and crystallizer by reducing the levels of calcium and magnesium in the wastewater stream.

Table 1
Typical Wet FGD Purge Stream Chemistry

Constituent	Concentration (mg/l)
Calcium	5,000
Magnesium	4,000
Sodium	2,000
Sulfate	2,000
Chloride	15,000
Fluoride	500
Arsenic	0.5
Barium	5.0
Cadmium	0.5
Chromium	0.5
Cobalt	1.0
Copper	2.0
Manganese	30
Mercury	0.02
Nickel	2.0
Selenium	4.0
Thallium	0.5
Total Suspended Solids	10,000

Note: Values in table do not consider the contributions of any absorber performance enhancing additives)

This licensing approach is normally considered a last resort in the design analysis for the power plant due to the high costs associated with the installation and operation of the ZLD equipment. Brine concentrators, evaporators, and crystallizers are constructed from expensive metals and metal alloys such as titanium, CD4MCu, Hastelloy C, 254 SMO, and AL6XN to help prevent scaling and plugging of the vessel internals. Operation of this equipment also requires low pressure steam for startup and/or continuous service if electrical-driven vapor compressors are not selected. Where steam is not

available for continuous operation of the equipment, mechanical vapor compressors driven by medium voltage motors consuming large amounts of electricity are utilized to power the ZLD equipment. For instance, on one recent project, a brine concentrator designed to concentrate 60 gpm of wastewater with a 95% recovery required a 350 hp mechanical vapor compressor for operation. Case Study #4 presents a situation in which ZLD was presented as the licensing approach for a new coal-fired power generating facility due to the limitations imposed on the plant to discharge any wastewater from the site.

FACTORS IMPACTING TECHNOLOGY SELECTION PROCESS

Ability to Obtain NPDES Discharge Permit for Stream

The ability of the Owner to obtain an NPDES discharge permit for ultimate disposal of the wet FGD purge wastewater is the most critical factor in the treatment technology selection process. Even though most discharge permits today are heavily restricted on the quality and quantity of wastewaters allowed for discharge, having the ability to discharge wastewater in some fashion from the facility opens up a much wider range of treatment options for the plant designer and plant owner. A discharge permit, however, does require constant regulatory surveillance and reporting of wastewater quality as negotiated with the regulating authorities.

There are numerous reasons why disposal of this FGD wastewater stream may not be an option. First of all, there may simply not exist a permissible location to discharge wastewater to a water body due to the location of the facility. Plants located in the southwestern US, for instance, typically encounter this problem where limited makeup water supplies may be available from area wells, local municipalities, or wastewater treatment facilities, but a local body of water into which the plant wastewater can be discharged does not exist. Another barrier to obtaining a discharge permit for this wastewater stream is the water quality of nearby bodies of water. Since this wastewater stream is very high in TDS and chlorides, these parameters may prevent obtaining a reasonable discharge permit for this wastewater stream. The situation is seriously impacted when the potential ultimate disposal source feeds into a water source that is a drinking water supply. A final and growing concern for owners attempting to obtain a NPDES permit for discharge of wet FGD purge wastewater is the

restraint on discharge of "ash contact wastewater" by some state authorities. Even though restrictions on discharging ash contact wastewater originally were designed to prevent the discharge of ash transport wastewaters (i.e. bottom ash sluice water), these limitations have expanded in some areas to include any wastewater streams that contact flyash or bottom ash such as storm water from ash areas and wet FGD purge wastewater.

Heavy Metals and Other Discharge Permit Limits

In addition to TDS and chlorides, the heavy metal constituents typical of a wet FGD purge wastewater stream may make obtaining an NPDES permit quite difficult. If the owner or developer is successful in obtaining a discharge permit in today's environmentally conscious world, the very low discharge limits of certain heavy metals commonly being enforced present treatment challenges.

The constituents of the wet FGD purge stream may vary considerably depending on coal, FGD reagents such as limestone, and wet FGD makeup water quality. The injection of performance enhancing additives into the wet FGD system may also impact the chemistry of this wastewater stream. Chlorides, fluorides, TDS, heavy metals, and organics are typically the parameters of interest in most recent NPDES permits. Of the various heavy metals typically present in the purge stream, mercury and selenium are normally the two metals that are heavily regulated, although arsenic, cobalt, cadmium, and thallium have also drawn the interest of some permitting authorities.

New Environmental Protection Agency (EPA) test methods allowing for very low level detection of mercury in water streams have helped to spark the regulation of very tight mercury limits in some recently issued discharge permits. EPA Method 1631E, approved for use in 2002 for instance, allows for detection of mercury in water down to 0.5 ng/l utilizing cold vapor atomic fluorescence spectrometry methods⁽³⁾. The Elm Road plant in Wisconsin withdraws and returns wastewater to Lake Michigan and has recently obtained a permit limiting mercury discharged from its facility to a maximum concentration of 1.3 ng/l. The plant NPDES permit allows for the treated wet FGD wastewater treatment system effluent to be combined with the condenser once through cooling water prior to the outfall location to meet the regulated mercury limits. At another facility withdrawing and returning water to the Ohio River, a mercury limit of 12 ng/l has been discussed by the

state regulators as a potential restriction, although this limit has not been currently imposed. The plant is currently permitted to discharge wastewater containing 1 µg/l maximum of mercury.

Selenium, like mercury and other heavy metals, is regulated by the EPA drinking water standards in many surface bodies of water. The United States EPA National Primary Drinking Water Standards currently limit selenium in bodies of water that supply drinking water to the public to 0.05 mg/l⁽⁴⁾. Due to the toxic effects that high levels of selenium have been demonstrated to have on both humans and wildlife, proposals have been made in some areas to restrict selenium discharges to 0.3 µg/l or lower. Although none of the case studies presented in this paper were subject to selenium discharge restrictions tighter than 2 to 3 mg/l, NPDES permit limits on selenium of 0.2 mg/l or less are quite common.

WFGD Scrubber Additives

Another factor that may have a large impact on the technology selection process for wet FGD purge wastewater treatment is the addition of organic compounds into the FGD scrubber vessel itself to improve performance of the FGD system. Some wet FGD equipment manufacturers have recently begun promoting the injection of DBA into their scrubber vessels touting SO₂ capture rates of greater than 99%. DBA is a biodegradable additive used in wet FGD scrubbers to reduce flue gas exit corrosion, reduce FGD reagent consumption, improve SO₂ reduction through ability to over scrub, and reduce scale and pluggage. The product is a blend of adipic acid, glutaric acid and succinic acid and is represented by the chemical formula: HOOC(CH₂)₂-₄COOH⁽⁵⁾. In the wet FGD scrubber system, DBA breaks down and is measured as BOD in the purge wastewater stream. The typical dosage rate of DBA can be 1000 mg/l or higher depending on the distinct characteristics of each individual system. Many facilities are restricted on BOD in their NPDES discharge permit; therefore, the DBA addition to the scrubber system will complicate and increase the cost of the purge treatment system requiring the inclusion of biological treatment units to reduce the level of organics in the wastewater stream.

In addition to adding organics to the wet FGD purge wastewater stream, DBA can also complicate the removal of heavy metals from the wastewater stream via physical/chemical precipitation processes. While laboratory studies have predicted that DBA addition will have little or no effect on

mercury removal, DBA addition has been observed to impact the removal of selenium from the wastewater stream. The addition of the organic compounds found in DBA to the absorber promotes the formation of selenium into selenate compounds which are not readily precipitated in physical/chemical treatment processes. If the power generating facility is subject to low level selenium restrictions in its discharge permit, biological treatment steps may be required to be included in the wastewater treatment system design to not only remove the organics, but to also convert the selenium into a form which can be precipitated easily.

Some DBA suppliers estimate that operational and maintenance costs of a typical wet FGD system can be reduced by around \$200,000/year by injection of DBA in the system through increased efficiency, decreased FGD reagent consumption, and lower power requirements ⁽⁶⁾. However, the additional capital and operational costs associated with the purge treatment system equipment need to also be taken into consideration when evaluating the total benefit achieved by installation of the DBA injection system.

Other additives that may potentially be introduced into the wet FGD scrubber system include organosulfide products added to enhance mercury removal from the flue gas and minimize mercury re-emission during gypsum by-product dewatering. Although not undesirable from a wet FGD purge wastewater treatment perspective, the organosulfides may add complexity to the overall control of metals precipitated in the clarification process due to chain reactions. Optimization of the chemical feed rate in the absorber vessel will need to be coordinated with selection and optimization of chemicals fed in the wastewater treatment process.

Air Pollution Control Systems Design

The constituents of the wet FGD purge stream as well as the quantity of the required purge steam will vary depending on the coal, limestone or other FGD reagent, and WFGD makeup water chemistries. Scrubber materials of construction will typically limit the chloride or fluoride concentration in the scrubber slurry to a set value. Limits of 15,000 mg/l chlorides and 600 mg/l fluorides are commonly implemented to control the material costs involved in design of the scrubber internals. With materials-based limits such as these in place, the higher the chloride and/or fluoride concentration in the coal and makeup water,

the greater the volume of scrubber purge water that will be required to be processed.

Whether or not the power plant facility intends to sell the gypsum by-product produced by the wet FGD system will also affect the design of the purge wastewater treatment system. Wallboard quality gypsum purchasers, for instance, typically restrict chloride concentration to a maximum of 150 mg/l. If the by-product gypsum is planned to be landfilled as opposed to being sold, the chloride concentration will simply be dependent on scrubber materials and, therefore, there will likely be a smaller purge stream from the scrubber that needs to be handled, treated, and disposed.

The design of other plant air quality control equipment can also impact the design of the wet FGD purge wastewater treatment system. For instance, a baghouse will typically do a better job of removing mercury from the flue gas stream than an electrostatic precipitator (ESP), removing approximately 60 to 80% of the influent mercury. Activated carbon injection upstream of the baghouse will further reduce the level of mercury in the gas stream. As is typical in any physical/chemical precipitation process, removal of contaminants is more difficult the lower the influent stream levels.

Opportunities for Recycle within the Power Plant

An evaluation of the potential opportunities for recycle of the treated or untreated wet FGD wastewater purge stream will provide valuable information that factors into the conceptual and final design of any treatment and disposal system for this waste stream. Potential recycling options in a coal-fired power plant may include ash conditioning, dust control, bottom ash cooling or transport, and cooling tower makeup. Effective management of the plant water balance and a sound water management administrative plan may substantially reduce or even eliminate the need for a permitted outfall for this wastewater stream. If not entirely eliminating the need for a permitted outfall, the ability to recycle the wastewater stream within the plant facility may be effective in reducing the overall cost and complexity of the purge wastewater treatment system. Recycled water for ash wetting, for instance, is likely to require a coarser level of treatment than wastewater treated for discharge to a surface water body.

Sludge Disposal Considerations

The availability of locations for disposing of the sludge produced by a physical/chemical precipitation process and the cost of the disposal (transport and landfill fees) should be factored in when selecting the optimal technology for treatment of the wet FGD purge stream. The quantity of sludge produced by the commonly utilized two stage hydroxide/carbonate and hydroxide/sulfide precipitation processes can be excessive and quite costly to dispose of if no suitable low cost disposal facilities exist nearby. For instance, a recently designed system that utilizes a two stage hydroxide/sulfide precipitation process to treat 250 gpm of wet FGD purge is anticipated to produce up to 63 tons/day of sludge. While the sludge cake produced via this precipitation process will pass the EPA Method 9095A paint filter liquids test as well as the Toxicity Characteristic Leaching Procedure (TCLP) in the vast majority of cases, rare instances may occur where the sludge fails these tests, is deemed toxic, and is required to be disposed of as hazardous waste.

Miscellaneous Criteria

Typically the design of a wet FGD purge wastewater treatment system is custom tailored to each individual plant's water management preferences and regulatory requirements; therefore, there are often other miscellaneous criteria that may factor into the technology selection process. Space constraints or the availability of relatively low cost land may promote the preference towards one technology or another. CWTS, for instance, require several acres of land per 100 gpm of wastewater required to be treated, while biological or physical/chemical precipitation processes can be accomplished with a much smaller footprint. Local political pressure may also influence technology selection. There may be outside pressure on an owner or operator to choose a very environmental friendly treatment process such as CWTS to satisfy local groups. Local political pressure can also force a plant to design utilizing a ZLD scenario in instances where it can be anticipated that no level of wastewater treatment will be found acceptable to local political or environmental forces. The location of the plant can also be an issue; CWTS are much more dependent on warmer climates to allow the wetlands to flourish, while other treatment systems are less dependent on ambient temperatures. Chemical handling and storage considerations may also factor into the decision making process. Physical/chemical precipitation processes require

the addition of numerous chemicals such as hydrated lime, hydrochloric acid, inorganic or organic sulfide products, and coagulants for process control. Biological and wetlands systems, on the other hand, typically require much less chemical feeds. Finally, owner preference and experience can greatly impact the technology selection process. An owner's or an engineer's positive or negative experience with handling and transfer of chemicals, a certain type of system design, or a particular equipment supplier at another facility or at a nearby facility may sway the decision toward or away from a particular treatment plan that is best suited for the process and would have been the optimal choice. The experience of the plant operators with certain treatment schemes may be a factor related to owner preference. For instance, if the plant operations staff has no history or experience with a biological treatment system of any sort, the owner may want to shy away from this technology, wary of the ability of his staff to successfully operate and control the treatment process.

CASE HISTORIES

The following case histories are presented to illustrate how various factors have impacted the design of wastewater treatment systems for wet FGD purge streams in practical applications. The first case study involves the retrofit of a wet FGD system on an existing multi-unit coal-fired power plant, while the remaining four cases are based on designs and licensing approaches presented for new green field power generating facilities.

Case Study #1

This case study involves a wet FGD retrofit on a multi-unit coal-fired power generating facility in Ohio that is currently under construction. The wet FGD purge wastewater stream is anticipated to vary between 105 and 250 gpm depending on the number of units in service and the coal blend that is burned by the plant. No additives, such as DBA, are designed to be added to the FGD absorber vessel. The wastewater stream is to be treated for discharge to the existing plant ash pond, which ultimately discharges to the Ohio River, utilizing the physical/chemical precipitation method commonly referred to as the alkaline sulfide process. In the alkaline sulfide process, metals are precipitated through two-stage clarification first as metal hydroxides and then as metal sulfides. The guaranteed wastewater treatment system discharge limits for the project are presented below in Table 2.

The NPDES permit modifications for the implementation of this new wastewater treatment system have not received final approval from the state at the present time. It is anticipated that the primary pollutant of concern in regard to the permit modifications will be mercury. A guarantee for less than 2 µg/l mercury in the wastewater treatment system effluent will enable the plant to meet the anticipated 1 µg/l mercury plant outfall limit when combined with other wastewater streams from the ash pond.

Table 2
Case Study #1 Wastewater Treatment System
Effluent Guarantees

Constituent	Concentration (mg/l)
pH	6 to 9
Turbidity, NTU	10
Total Suspended Solids	10
Aluminum	5.0
Antimony	0.5
Arsenic	0.3
Barium	5.0
Beryllium	0.2
Cadmium	0.5
Chromium	0.5
Cobalt	1.0
Copper	1.0
Fluoride	500
Iron	0.5
Lead	0.7
Manganese	3.0
Mercury	0.002
Nickel	2.0
Phosphorus, as P	1.0
Selenium	3.0
Thallium	0.5
Tin	0.5
Zinc	4.0

Case Study #2

Case Study #2 involves the design of two new 900 MW pulverized coal-fired units on a green field site in the Midwestern United States. The project is currently in the engineering and procurement phases. The power plant NPDES permit does not allow for discharge from the site of ash contact water which, in this case, includes wastewater purged from the wet FGD system. The coal at this facility is very high in fluoride content, which is thus the limiting factor driving the amount of purge required from the wet FGD absorber as well as the materials of

construction for the FGD system components. Early estimates of the wet FGD purge water stream required to maintain acceptable fluoride levels in the FGD system were up to 350 gpm per unit.

Optimization of the system design involved investigating potential avenues for reducing the amount of required purge from the wet FGD absorber to allow reuse of the entire purge stream as ash conditioning water in the pugmills. The agreed upon solution involves treating the approximately 700 gpm of wet FGD purge water to reduce the level of fluorides from 500 mg/l to about 20 mg/l and returning the majority of the treated wastewater stream to the wet FGD system as makeup to the absorber vessel. Approximately 85 gpm of treated wastewater stream will be withdrawn from the loop and disposed of with the ash as stabilization water controlling the chloride level in the wet FGD system to 20,000 mg/l. The predicted wastewater treatment system influent water and the desired treatment system effluent quality are presented below in Tables 3 and 4.

Table 3
Case Study #2 Wastewater Treatment System
Predicted Influent

Constituent	Concentration (mg/l)
pH	5.0 to 6.5
Calcium	10,000
Magnesium	7,000
Sodium	2,800
Sulfate	2,500
Chloride	20,000
Fluoride	500
Total Dissolved Solids	30,000 to 90,000
Total Suspended Solids	10,000

Table 4
Case Study #2 Wastewater Treatment System
Design Effluent

Constituent	Concentration (mg/l)
pH	6.0 to 9.0
Fluoride	20
Total Suspended Solids	10

Case Study #3

This case study involved a licensing scenario in which the reuse of the treated wet FGD wastewater stream as makeup for the cooling tower was evaluated. The case study involves the conceptual design calculations for the licensing application for

one 900 MW pulverized coal-fired power plant to be located on a site in the eastern United States. The wet FGD purge wastewater stream was anticipated to be approximately 125 gpm based on preliminary fuel quality information. No additives, such as DBA, were anticipated to be added to the FGD absorber vessel. The wastewater stream was to be treated using the alkaline sulfide physical/chemical precipitation process. The treated wastewater stream would be recycled as makeup to the plant cooling tower as it was anticipated that a separated outfall for this wastewater would not be able to be permitted and no other potential users of the wastewater stream were viable alternatives. Normal cooling tower makeup was to be partially softened and clarified mine drainage water. Chlorides in the wet FGD absorber were to be limited to 15,000 mg/l. No PM₁₀ air regulations on TDS were anticipated.

Cooling tower circulating water chemistry based on 125 gpm of treated wet FGD purge wastewater recycled to the cooling tower and 7 cycles of concentration (COC) in the cooling tower was as presented below in Table 5.

Table 5
Case Study #3 Predicted Cooling Tower Chemistry

Constituent	Concentration (mg/l)
Arsenic	0.03
Chloride	1614
Copper	0.02
Mercury	0.0012
Selenium	0.04
Zinc	3.01
Total Dissolved Solids	9230

Condenser tube materials and other system metallurgy would be required to be 317 SS or better based on this anticipated cooling tower chemistry. Condenser tube material selection in this case was impacted by the addition of the recycled wet FGD purge water to the cooling tower basin. Without the addition of the recycled wastewater to the system, the chloride content of the circulating water would have been less than 150 mg/l, allowing the usage of 304 or 316 SS materials.

Case Study #4

Case Study #4 involved a licensing scenario in which no viable discharge alternatives were available for disposal of any of the plant wastewater which, therefore, necessitated proceeding with the design of the power generating facility as a ZLD

facility. This case study involves preliminary design calculations for a 2 x 750 pulverized coal-fired power plant to be sited in the southwestern United States. Due to the lack of viable water sources in the area, the plant was designed to utilize air-cooled condensers for cooling the condensed steam from the steam turbines. Makeup water to the wet FGD system was designed to be both fresh water from nearby wells and recycled low TDS plant wastewater.

The purge stream from the wet FGD system, anticipated to be approximately 120 gpm per unit, was to be combined with other high TDS plant wastewater sources and treated for hardness and suspended solids reduction in a clarifier prior to concentration in the brine concentrator. The distillate from the brine concentrator was to be reused as makeup to the wet FGD system (low TDS wastewater) and the concentrate stream was to be utilized for by-product stabilization. Since the concentrate from the brine concentrator was estimated to be approximately 1/10th of the amount of water required for by-product stabilization, the slurry-like concentrate from the ZLD brine concentrator would be mixed with other plant wastewater streams in the by-product stabilization system.

Case Study #5

Case Study #5 involves the design of the wet FGD wastewater treatment system for the Elm Road Generating Station located in Wisconsin just south of the city of Milwaukee. This project consists of two new 680 MW pulverized coal-fired units and is currently in the construction phase. The plant utilizes water from Lake Michigan for its once-through condenser cooling water system at a flow rate of about 540,000 gpm. The wet FGD purge wastewater stream is estimated by Alstom, the FGD supplier, to be a maximum of 275 gpm total for both units. No additives are designed to be added to the FGD absorber vessel.

The state of Wisconsin has a "Mercury Emission Reduction Program" in which the state proposes to reduce mercury emissions by 90% over the next decade. The state has been examining all of the sources of mercury released into the environment and attempting to make reductions in each source. Power plant discharges represent a large point source and have been a focus of their reduction efforts. As a result of these efforts, the Elm Road NPDES permit includes a mercury discharge limit at the bio-toxicity limit for mercury which is 1.3 ng/l.

The bio-toxicity is the limit at which it has been determined that accumulations will not present a hazard in biological organisms up the food chain. However, this limit is imposed at the “end of pipe” at the plant common outfall, which allows the plant to mix the effluent from their FGD wastewater treatment system with once-through condenser cooling water prior to discharge via the plant outfall.

To remain below the 1.3 ng/l mercury limit it was determined that the FGD wastewater treatment system would be required to be designed to produce an effluent containing a maximum of 0.2 µg/l of mercury. The process chosen to achieve this limit was the alkaline sulfide process. The guaranteed wastewater treatment system discharge limits for the project are as presented below in Table 6.

Table 6
Case Study #5 Wastewater Treatment System
Effluent Guarantees

Constituent	Concentration (mg/l)
pH	6 to 9
Turbidity, NTU	5
Total Suspended Solids	1
Aluminum	5.0
Antimony	0.5
Arsenic	0.3
Barium	5.0
Beryllium	0.2
Cadmium	0.5
Chromium	0.5
Cobalt	1.0
Copper	1.0
Fluoride	500
Iron	0.5
Lead	0.7
Manganese	3.0
Mercury	0.0002
Nickel	2.0
Phosphorus, as P	1.0
Selenium	3.0
Thallium	0.5
Tin	0.5
Zinc	4.0

CONCLUSIONS

Given the numerous issues that can factor into the wet FGD purge wastewater treatment system technology selection process, the design of this treatment system for each power generating station is essentially a custom design based on that site's particular characteristics and licensing scenario.

When developing a licensing approach for a new plant or for a wet FGD retrofit on existing units, the plant designer and/or plant owner needs to carefully consider the various treatment options available to him or her given the current local attitudes towards waste streams of this nature as well as potential future changes in regulations, particularly in the areas of heavy metals discharge or disposal. Despite the strict environmental discharge regulations that are coming into play in many areas of the United States and other countries, numerous options are available to the plant designer and/or plant owner to deal with this wastewater stream as exemplified in this technical paper.

REFERENCES

1. Sinha, Kumar, Colleen Layman, and Colleen Chapman (2007). *Environmentally Acceptable Treatment Options for FGD*. Electric Power 2007 – Chicago, IL.
2. Rodgers, John H., George M. Huddleston III, Cynthia Murray-Gulde, and F. Douglas Mooney (2005). *Designing Constructed Wetlands for Mitigating Risks from Flue Gas Desulfurization Wastewater*. International Water Conference IWC 05-70 – Orlando, FL.
3. Environmental Protection Agency (EPA) 2002. *Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*. Office of Water. EPA-821-R-02-019.
4. Environmental Protection Agency (EPA) 2003. *National Primary Drinking Water Standards*. Office of Water. EPA 816-F-03-016.
5. Invista Specialty Intermediates (2005). Technical Datasheet – Dibasic Acid (DBA).
6. Invista Specialty Intermediates (2005). *The Role of Dibasic Acid (DBA) in Wet Limestone Flue Gas Desulfurization*. Downloaded from: http://intermediates.invista.com/e-trolley/page_1035/index.html