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Wastewater Treatment for FGD Purge Streams

Paper # 33

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ABSTRACT

In developing a wet limestone flue gas desulfurization (FGD) retrofit program, utilities must also develop a strategy for the associated wastewater treatment system (WWTS) to treat the scrubber chloride purge stream. This purge stream is required to control chloride concentrations and solids fines build-up in the scrubber.

In this paper, characteristics of FGD purge streams will be identified and items affecting those characteristics will be discussed, including the coal source, limestone quality, scrubber design, and makeup water quality. Key elements affecting the design and sizing of FGD wastewater treatment systems will also be discussed. A number of case studies will be presented to illustrate different wastewater treatment systems that resulted from the combination of the FGD purge characteristics and the final treated effluent requirements. Operational procedures and system flexibility for future changes will be covered. Lessons learned will be presented on systems currently in operation, as well as some under construction or design.

INTRODUCTION

Flue gas desulfurization continues to be a topic of current interest as many utilities are engaged or have completed retrofit projects to meet emissions standards from Phase 2 of the Clean Air Act. A large number of the projects are underway and will be completed in the time frame of 2006–2011; however it appears retrofits will continue to be made as late as 2015–2020. A significant number of the FGD projects are wet limestone forced oxidation (LSFO) scrubbers.

To maintain the required operating conditions in the scrubber, a purge stream is discharged from the scrubber system primarily for chloride control (for compatibility with the scrubber's materials of construction and to achieve SO_2 removal efficiency). Sometimes the purge stream is necessary for fines control in the absorber. The FGD purge stream contains pollutants from coal, limestone, and make-up water. It is acidic, supersaturated with gypsum, and contains high dissolved solids and suspended solids, comprised of, in addition to gypsum, heavy metals, chlorides, magnesium, and dissolved organic compounds. "Heavy metals" is a term that refers to a broadly defined group of elements that exhibit metallic properties, including transition metals, metalloids, lanthanides and actinides.[1] A subset of the heavy metals is usually the focus of NPDES permits and of the performance requirements of wastewater treatment systems for FGD purge streams.

For some plants located on large rivers or water bodies, it is permissible to direct the FGD purge to the ash pond for suspended solids settling, pH adjustment, and dilution of the heavy metals concentrations simply by mixing the smaller FGD purge with ash pond water. For these plants, the ash pond discharge stream meets the NPDES permit requirements for discharge.

More commonly, treatment of the purge is required prior to discharge to the receiving water body. This is often the case even for plants that have once-through cooling water systems available for co-mixing and which discharge to large rivers. A number of options may be considered:

- Physical/ chemical treatment to reduce total suspended solids, adjust the pH, de-supersaturate the stream, and reduce heavy metals. This is the most commonly used system in current FGD retrofit programs with about 15 systems installed and operating since 2004 and over 25 under construction in the United States.

- Biological treatment to reduce selected heavy metals, and/or COD/BOD_5, and/or total nitrogen. Used in selected plants to reduce selenium to low levels,[2] to reduce COD/BOD_5 resulting from use of organic acids, or to reduce total nitrogen[3] (usually due to ammonia slip from an SCR unit). A biological system is usually be preceded by a physical chemical system. About eight biological systems have been installed or planned for installation since 2004.

- Zero liquid discharge with thermal units (evaporator, crystallizer, spray dryer). Only one operated in the U.S. briefly in 1990s with multiple challenges of scaling, corrosion, and high costs.[4] Two more have been ordered in recent years, with one in construction and one cancelled during construction.[5] Some installations overseas are installed or under construction – no report on performance yet.

- Zero liquid discharge with deep well injection. Only one in operation in the U.S. and one in construction.[6] This option has a fairly high capital cost ($5–6 million per well, with two to three wells per site.) Deep well injection still requires a physical chemical treatment system preceding it to de-supersaturate the wastewater to prevent scaling in the high temperature, high pressure deep well environment.

- Sludge stabilization by mixing FGD purge with fly ash for land filling. None currently being built, however about 15 were constructed in the 1970/80s. This approach eliminates the ability to sell fly ash used for commercial products and requires extra landfill volume. At one power plant, this option was considered but availability of sufficient fly ash quantities could not be assured.

- Stacking the gypsum for either final disposal or future reclaim will absorb some of the purge in the stack. Runoff of excess liquid is collected in holding basins or mixed with ash water. A couple of these designs are under construction.

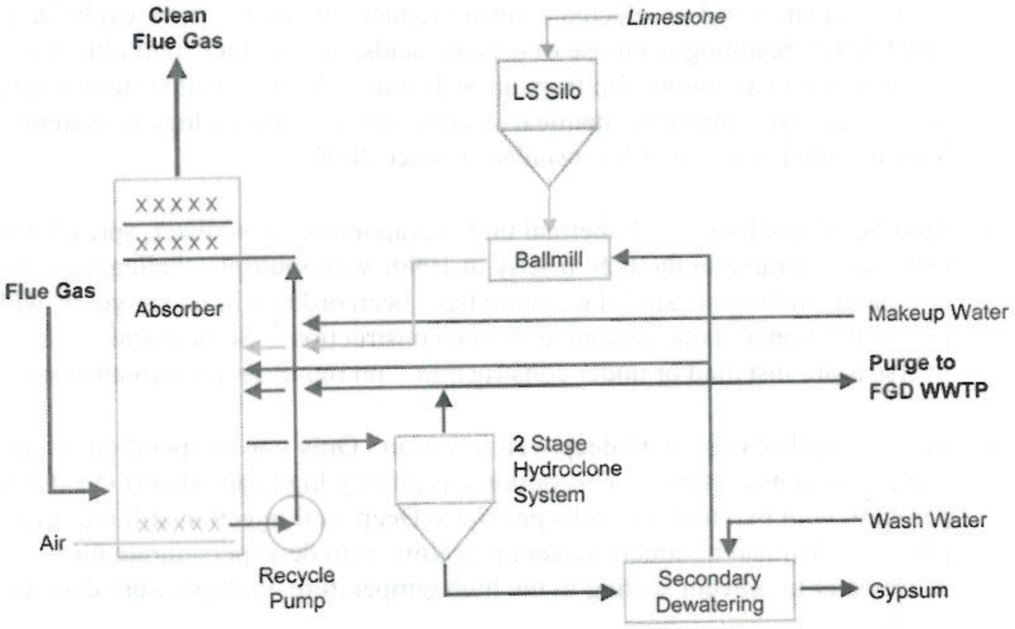
- Constructed wetlands – biological process. Three have been completed with mixed results.[7,8]

Of all of these treatment processes, the most commonly used is the physical/ chemical system, which will be the primary subject of this paper.

CHARACTERIZATION OF FGD WASTEWATER

The FGD wastewater to be treated comes from the hydroclones of the gypsum dewatering system, as depicted in Figure 1.

Figure 1: Simplified Limestone Forced Oxidation (LSFO) FGD Water Balance



FGD wastewater composition can vary from plant to plant, as depicted in Figure 2. The wastewater flowrate and characterization are affected by the coal burn rate, scrubber equilibrium chloride concentrations, efficiency of fly ash removal, type and efficiency of the gypsum dewatering system, type of FGD process used, and composition of the coal, limestone and make-up water.

The purge rate required to maintain a target equilibrium chloride concentration is directly dependent on the coal chloride content and coal burn rate. Powder River Basin (PRB) coals generally have much lower chloride content than Eastern Bituminous coals. Therefore, for a given target equilibrium chloride concentration, the concentrations of metals in the FGD wastewater will tend to be higher for systems burning PRB coals versus Eastern Bituminous Coals. Also, for a specific power plant, if the coal burned has a lower chloride content than the design basis coal, the scrubber might be operated at a chloride purge rate lower than the design value, which could result in higher concentrations of other constituents. The increased concentrations can be significant for some metals, such as selenium, whose concentration in the treated wastewater is dependent on the influent concentration and not just dependent on solubility of metal compounds. This impact of coal chloride content on predicted concentrations of constituents of the chloride purge (for a target equilibrium chloride concentration) and on changes in purge flow rate and characterization, due to changes in the actual coal chlorine content, are nearly independent of the coal sulfur concentration.

In addition to the variations in untreated wastewater characterization, the discharge limits can also vary significantly from plant to plant, dependent upon the state in which the plant is located, the availability of an existing high flow rate discharge stream (e.g., once-through cooling water), the nature of the receiving body of water, and the year in which the FGD system goes into service. Plants retrofitting later appear to have more stringent NPDES permit requirements for the FGD wastewater compared to earlier plants within the same regulatory region. Systems have varied in size from 20 gpm to 1,200 gpm. The table below depicts the purge characteristics (as specified) and discharge limits for three plants. This indicates the variety of both purge and discharge characteristics and the fact that some specified purge constituents are not reported (NR) for some plants and many constituents are not applicable (NA) for the discharge limits at some plants. Thus, each plant will have their unique specified purge and discharge limits.

Table 1: FGD Wastewater Characteristics and Discharge Requirements for Three Representative Plants (different than the case study plants later in paper)

	Plant 1		**Plant 2**		**Plant 3**	
Parameter	**Specified Purge**	**Discharge Limits**	**Specified Purge**	**Discharge Limits**	**Specified Purge**	**Discharge Limits**
pH (S.U.)	5.0 to 6.0	6.5 – 9.0	5.5 – 6.5	6.5 – 8.0	5.5 – 65	6 - 9
Temp (°F)	125	NA	125	NA	130	
Constituents	**ppm**	**ppm**	**ppm**	**Ppm**	**ppm**	**ppm**
TSS	≤18,000	<10	<15,000	30	20,000	15
TDS*	40,000	40,000	30,000	NA	NR	NA
Chloride*	15,000	15,000	15,000	NA	15,000	NA
Total Nitrogen	NR	NA	81	10	NR	NA
Aluminum	10	1.5	12	2	14	2
Antimony*	0.55	0.55	0.55	NA	0.2	0.2
Arsenic	1.5	0.1	3	NA	3	0.1
Barium*	4	4	NR	NA	0.004	0.004
Beryllium*	0.1	0.1	0.1	NA		
Boron*	300	NA	NR	NA	600	600
Cadmium	0.45	0.1	0.5	0.03	0.5	0.1
Chromium, total	0.3 (Cr3+)	0.1	0.5 (Cr3+)	0.1	1	0.1
Cobalt	0.2	0.1	0.2		0.2	0.1
Copper	0.85	0.1	0.2	0.1	0.8	0.1
Iron	20 (dissolved)	0.5	20	1	NR	NA
Lead	0.5	0.1	4	0.1	4	0.1
Magnesium	1,500	NA	1,500	NA	7,000	7,000
Manganese	NR	NA	NR	NA	300	3

Mercury	0.5	0.002	0.8	0.001	0.8	0.001
Molybdenum	0.25	0.25	NR	NA	NR	NA
Nickel	2	1.0	5 (90% particulate)	0.3	6	1
Selenium	4.6	3	5		5	2.835
Silver	0.3	0.02	0.3	0.05	0.03	0.05
Thallium*	0.2	0.2	0.1	NA	0.1	0.1
Vanadium*	1.425	1.425	1	NA	1	1
Zinc	5	0.1	5	0.1	8	0.1

* Parameters not impacted by physical chemical treatment, however some residual treatment can occur.

TREATING THE FGD PURGE STREAM

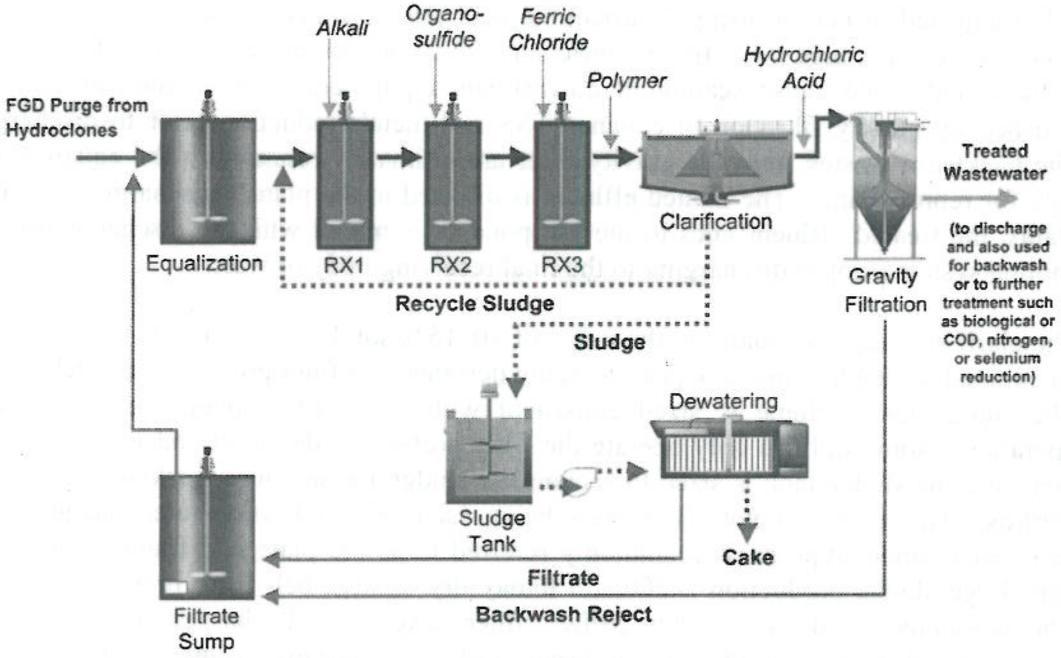
The scrubber purge stream is treated in a dedicated wastewater facility, rather than an existing treatment system, for the following reasons:

- The power plant's existing wastewater treatment facility may not have adequate capacity for the additional FGD purge flow.
- The materials of construction of the existing treatment facility most likely are unsuitable for treating a high chloride stream common to FGD wastewaters.
- The high TDS and supersaturated conditions of the FGD wastewater may result in scaling if the existing system does not have the correct chemical regime throughout.
- The treatment facility's process design may not be adequate for the very strict wastewater discharge limits likely to be enforced for the FGD wastewater.
- The quantity of additional sludge generated by treatment of the FGD wastewater may exceed the sludge and solids handling capacity of the existing system.

The specific FGD wastewater treatment system must be designed to meet the current wastewater composition and discharge requirements, but also have some flexibility for meeting future requirements either as designed and constructed or with hopefully minor modifications or add-ons to the system.

A basic building block in the WWTS has been an integrated physical/ chemical treatment system, as represented in Figures 2, 3, and 4. From a two stage hydroclone system, the stream will contain about 0.5–2% suspended solids (including gypsum and fines of un-reacted or inert materials) and be directed to an equalization tank, which provides a means to attenuate the flow and chemistry of the purge.

Figure 2: Process Flow Diagram of Typical Physical Chemical Treatment System with Three Stage Reaction



The wastewater is pumped to reaction tank #1 for addition of alkali (usually hydrated lime) for pH adjustment to about 8.5–9.2 and gypsum de-supersaturation of the wastewater. Proper control of the pH is essential to optimize the effectiveness of the other chemicals added for precipitating heavy metals. Also, it is important to not allow the pH to go higher than 9.2 to avoid magnesium precipitation, which would greatly increase the total amount of solids to be dewatered, impact dewaterability, and greatly increase scaling potential in the system. Recycle of sludge from the downstream clarifier provides seed crystals for gypsum growth to aid in the de-supersaturation process, which is critical to prevent scale from forming on the downstream equipment. Addition of the alkali also causes precipitation of abundant metals, such as aluminum, iron and manganese as metal hydroxides.

Some heavy metals will precipitate as hydroxides in this reaction step; however metal sulfides have much lower solubility than metal hydroxides. Thus, in order to meet the low effluent requirements for heavy metals, an organo sulfide is dosed into the stream in reaction tank #2 to further precipitate many of the heavy metals.

For enhanced coagulation, an iron salt such as ferric chloride is added in reaction tank #3. The iron salt helps denser flocs to form, thus improving clarifier performance. In addition, the iron salt will co-precipitate other metals, some non-metals and some organic matter.

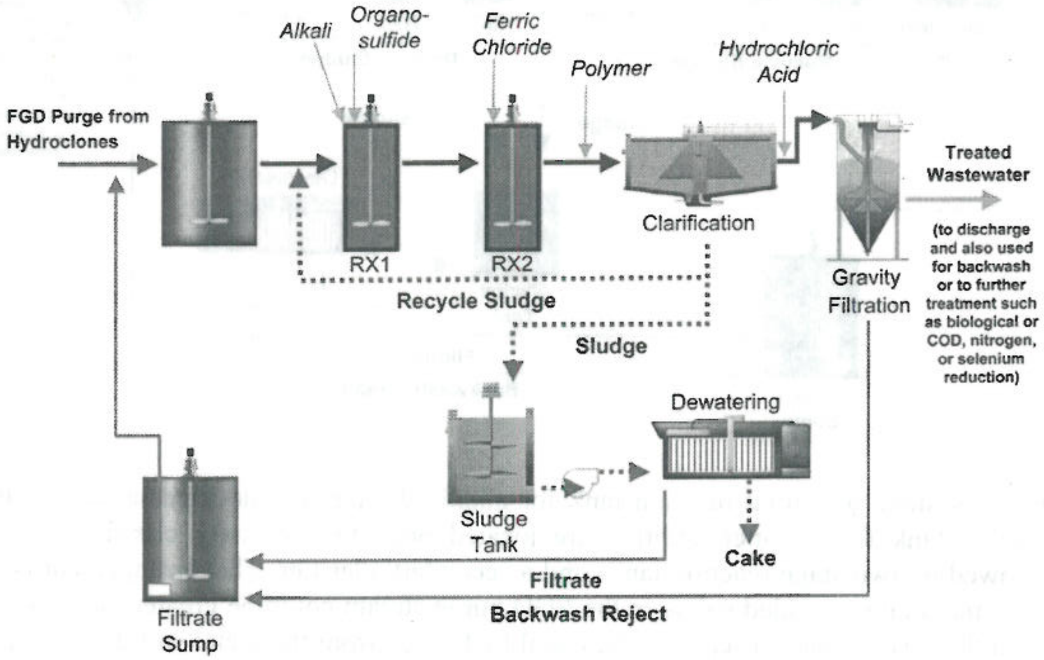
After the coagulation step, polymer is added in a mixing zone in the clarifier to aid in coagulation and solids settling in the clarifier. The wastewater undergoes clarification using a solids contact clarifier, in this particular process design. After clarification, the pH is adjusted to neutral using hydrochloric acid (HCl), which is used rather than less expensive sulfuric acid (H_2SO_4). Sulfuric acid would add to the saturation of the treated effluent and could cause scaling in downstream equipment. The treated effluent is polished by gravity filtration to enhance TSS and metals reduction prior to discharge. The backwash wastes from the gravity filter are ultimately returned to the equalization tank for reprocessing. The treated effluent is directed to the plant's discharge. In some plants, the treated effluent goes to the ash pond or is mixed with the discharge from a cooling system prior to discharging to the final receiving body of water.

The clarifier sludge is usually in the range of 10–15% solids by weight. It is pumped to an agitated sludge holding tank prior to being dewatered in filter presses on a batch basis. The sludge tank volume is sized consistent with the utility's plans for filter press operation. Some utilities only operate the filter presses on day shift and weekdays. In that case, the sludge tank is sized to accumulate sludge for an entire weekend or holiday periods. The most common filter press being used for FGD wastewater sludge is the recessed chamber type press (commonly referred to as the plate and frame type). For very large sludge production (>200,000 lb/day dry solids), belt filter presses are used. The dewatered solids (commonly called "filter cake") are discharged from the filter presses at 40–50 wt% solids and are disposed of in non-hazardous lined landfills, either onsite or offsite. The dewatered solids are generally required to pass the EPA "Paint Filter Liquids Test" and their leachate should meet Federal regulations regarding toxicity, in order to be considered non-hazardous. The dewatered solids are discharged either to portable containers ("roll off boxes") or can be discharged directly into a truck. Considerations for the method used include: frequency of filter press operation, cost of truck operation, and noise (the sound of roll off boxes may be objectionable if the plant is located close to a residential area).

Dependent upon the discharge permit for the power plant, additional treatment may be required downstream of the physical/ chemical treatment system. Some state or regional requirements (such as the Chesapeake Bay Initiative) limit total nitrogen in the discharge. The source of the nitrogen in FGD purge is usually ammonia slip from an SCR unit. Some states limit selenium on selected streams (North Carolina), and others limit the organic load (COD/BOD) created by use of dibasic acid or other organic acids in the scrubber operation. To reduce these contaminants to acceptable levels, a biological treatment system is incorporated after the physical/ chemical system. These biological systems include sequencing batch reactors for nitrogen and COD/BOD reduction at power plants located on the Chesapeake Bay watershed or fixed film biological treatment systems for selenium reduction at plants in North Carolina. The physical/ chemical system is still needed to perform the tasks of pH adjustment, de-supersaturation, suspended solids reduction, and removal of heavy metals. If these tasks were not accomplished, the biological systems would not operate properly and in many cases would scale from saturated conditions or be overloaded by the suspended solids.

Variations of the physical/ chemical treatment system may be used, including:

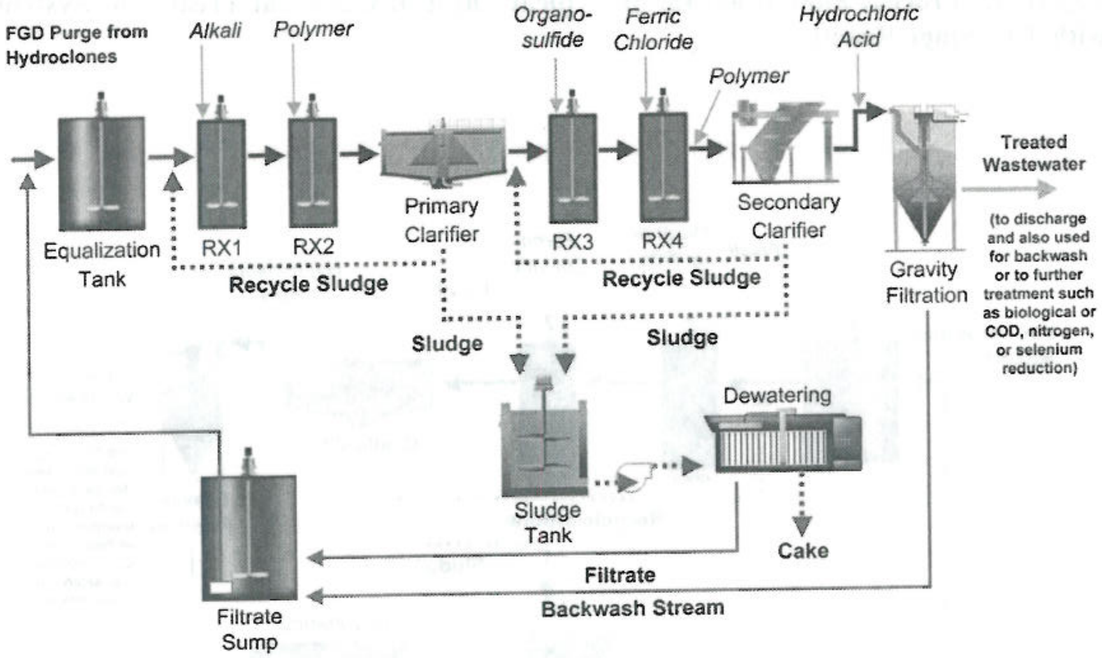
Figure 3: Process Flow Diagram of Typical Physical Chemical Treatment System with Two Stage Reaction



This design is very similar to the system in Figure 2, except that the alkali and organo sulfide are added to the same reaction tank sized with adequate retention time in the reaction tank for both chemicals to react with the wastewater for their intended functions.

The two stage reaction design treatment configuration, depicted in Figure 3, has become the preferred arrangement due to its efficiency, cost effectiveness, and reduced maintenance requirements.

Figure 4: Process Flow Diagram of Typical Physical Chemical Treatment Process with Primary and Secondary Clarifiers



In this system, an initial reaction tank for alkali addition and de-supersaturation and a reaction tank for polymer addition are located prior to a primary clarifier, which is followed by two stage reaction tanks and a secondary clarifier. This arrangement is used when the total suspended solids in the FGD purge stream could be greater than 2 wt% or when there is a desire to separate the metal hydroxide from the metal sulfide precipitated solids or when additional periodic blowdown for fines control occurs. However, for the case in which suspended solids may be higher than 2 wt% it usually would be more cost effective to ensure a second stage of hydroclones was included in the gypsum dewatering system, than to have a primary clarifier. If more than 2 wt% solids are forecasted in the flow to the WWTS, this likely indicates some gypsum product is unnecessarily being lost with the wastewater and the gypsum dewatering system should be tightened up. This design was used in European power plants in the 1970s-1980s (ref 9) and is more complex to operate and expensive than the configuration shown in Figure 3.

Another application of this arrangement would be if other plant streams, such as coal pile runoff and general drainage, are directed to the FGD WWTS. This situation may occur in a new power plant with FGD, where the wastewater treatment system is not dedicated to only FGD purge.

Case Study 1: We Energies Pleasant Prairie Power Plant (PPPP)

We Energies began operation of its Unit 1 wet limestone forced oxidation FGD and SCR systems in November 2006 at the Pleasant Prairie Power Plant (PPPP) in Wisconsin. Unit 2 FGD operation began in April 2007. A SCR unit had previously been installed on Unit 2. PPPP burns PRB coal and has been selling commercial grade gypsum produced by the FGD system since January 2007. FGD blowdown (to remove fines and chlorides) from two 600 MW scrubbers is treated using the alkali-sulfide process to achieve very low levels of mercury and other heavy metals. More detailed information on PPPP has been presented earlier (ref. 10).

URS-Washington Division provided overall Engineering / Procurement / Construction (EPC) services and Siemens Environmental Systems and Services (formerly Wheelabrator) supplied the FGD scrubber equipment. FGD chemistry mass balance modeling used factors such as coal, flue gas, limestone, and makeup water characterization, scrubber performance, materials of construction, and gypsum quality to determine the design requirements of the FGD wastewater treatment system (WWTS).

The WWTS design was based on a blowdown composition of 13,000 ppm chloride, 1.5% solids, and a flowrate of 75 gpm to provide operational and maintenance flexibility. Total mercury concentration in the PPPP FGD absorber blowdown was predicted to be as high as 2,000 ppb. The concentration of mercury in the FGD wastewater effluent would need to be significantly reduced to meet expected discharge limits, so mercury removal became the focus for the WWTS design.

In addition to the usual permit limits on total suspended solids, oil and grease, and pH, new limits were set by the Wisconsin Department of Natural Resources, as follows:

Table 2: New Discharge Limits for Pleasant Prairie Power Plant

Parameter	Location	Limit	Frequency
Mercury	WWTS effluent	1.5 µg/L (ppb)	2/Week grab
Mercury	WWTS effluent	0.00135 lbs/day	2/Week calculated
Mercury	Discharge to lake	80 ng/L (ppt)	2/Week grab
Arsenic	Discharge to lake	Monitoring only	Monthly composite
Beryllium	Discharge to lake	0.084 µg/L (ppb)	Monthly composite
Chloride	Discharge to lake	1514 mg/L (ppm)	Monthly composite
Copper	Discharge to lake	117 µg/L (ppb)	Monthly composite
Selenium	Discharge to lake	550 µg/L (ppb)	Monthly composite

Note: The selenium limit was added in early 2008 as a result of startup sampling performed in November and December 2007.

The discharge permit allows FGD wastewater only to be discharged when it is combined with cooling tower blowdown, coal pile runoff or other treated wastewater streams to ensure that mercury, chloride, and other parameters remain below the discharge permit limits. An operational limit has been established that requires a minimum of 1,500 gpm of cooling tower blowdown or other treated wastewater discharges to allow up to 50 gpm of FGD wastewater discharge.

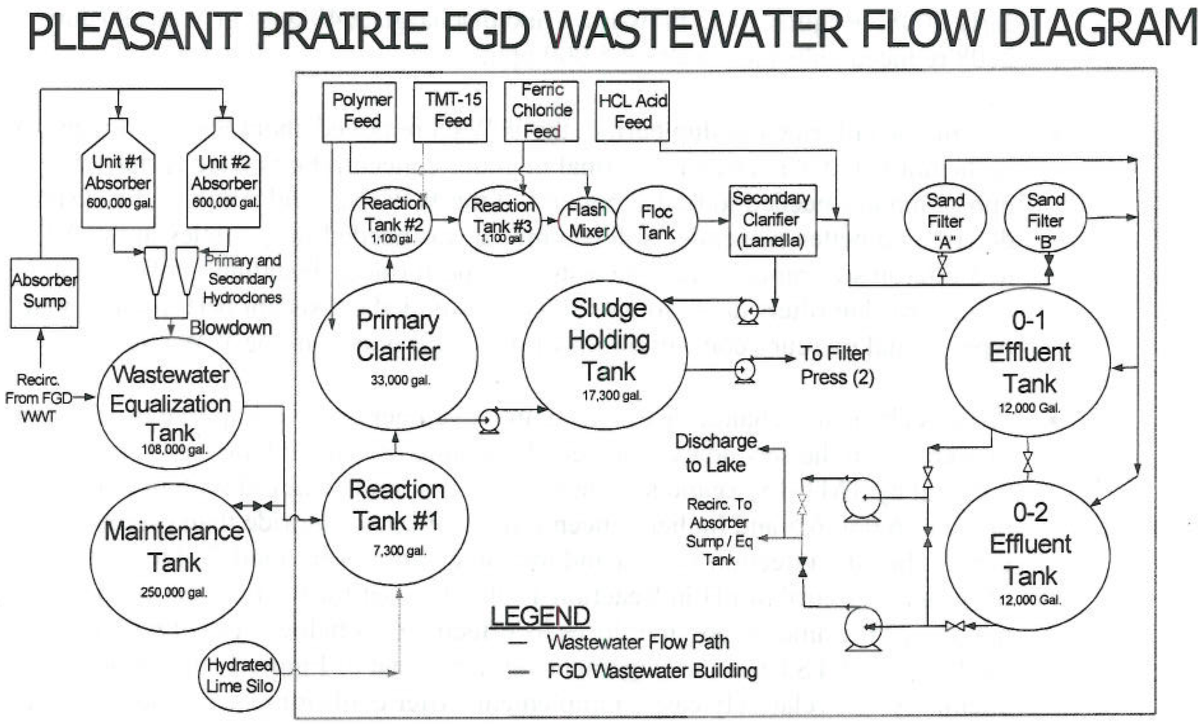
Table 3: Characteristics for Pleasant Prairie Power Plant WWTS

Parameter	Units	Specified Purge	Discharge Requirements
Total Suspended Solids	ppm	15,000 (1.5%)	15
pH	std. units	5.5 – 6.5	6 – 9
Oil and Grease	ppm	ND	10
Alkalinity	ppm	100 as CaCO3	NA
Arsenic	ppm	3.0	0.010
Antimony	ppm	0.200	0.100
Beryllium	ppm	0.004	0.0004
Cadmium	ppm	0.500	0.100
Calcium	ppm	10,000	n/a
Chlorides	ppm	15,000	15,000
Chromium	ppm	5.0	0.100
Copper	ppm	0.850	0.100
Lead	ppm	4.0	0.100
Magnesium	ppm	7,000	n/a
Mercury, Total	ppm	< 0.100 ≥ 0.100 < 0.800 ≥ 0.800 < 2.0	0.0002 0.0005 0.0015
Nickel	ppm	6.0	1.0
Selenium	ppm	3.0 (> 80% as selenite - Se^{IV})	2.5
Silver	ppm	0.300	0.300
Sulfate	ppm	2,200	n/a
Zinc	ppm	8.0	0.100

FGD Wastewater Treatment System Design

Siemens Water Technologies Corp. (formerly USFilter) was selected to design and provide the engineered equipment for the PPPP alkali-sulfide FGD WWTS. URS-Washington Division installed the system and provided system startup activities. Below is the process flow of the FGD WWTS.

Figure 5: Pleasant Prairie Power Plant WWTS



This design includes two stages of clarification and three chemical addition/reaction tanks to accomplish the wastewater treatment. The WWTS is design to process up to 75 gpm of FGD purge at a maximum suspended solids concentration of 1.5%. Accounting for filtrate recycle volumes, the design flowrate into Reaction Tank 1 is 19 to 94 gpm. Sizing of the individual tanks and clarifiers was based on a nominal 50 gpm system flow.

FGD WWTS Startup, Operating Experience, and Lessons Learned

Upon startup of the Unit 1 FGD scrubber in November 2006, the WWTS was operated with all treated FGD wastewater and filtrate returned to the absorbers (closed loop operation) until system performance met discharge permit requirements. Dewatered sludge from the primary and secondary clarifiers was confirmed as non-hazardous material and placed in on-site landfill storage. Lessons learned from the startup and performance testing periods include:

- To better control foaming in the scrubber, the WWTS was operated in early 2007 to remove smaller fines (<10 microns) in addition to adding a silicon-based antifoam agent to the scrubber and installing water sprays in the stilling well and absorber overflow.

- Absorber chloride levels increased to 12,000 ppm by late August 2007, because the absorbers were operated with no chloride purge by returning all treated FGD wastewater and filtrate to the absorbers. Semi-continuous FGD blowdown began in November 2007, and chlorides were control between 8,000 to 12,000 ppm in early 2008. Regular FGD blowdown and discharge at 40 gpm in May and June 2008 reduced chlorides to about 5,000 ppm.

- During the chloride buildup period, the WWTS removed about 99.5% of mercury in the untreated wastewater, but final mercury concentrations were about 3 to 5 ppb. Mercury needed to be 1.5 ppb out of the WWTS. Evaluation of the system determined better suspended solids removal was needed for particles in the 0.45 to 5 micron size range. Multiple tests were performed. Installation of absolute rated cartridge filters down to 0.45 micron provided consistent performance with typical final mercury concentrations of 0.2 to 1.0 ppb from the WWTS.

- Process chemistry changes were made in November 2007 to improve the removal of mercury in the secondary clarifier. Jar testing determined the best mercury removal by TMT-15 organo sulfide precipitation was achieved with pH in the range of 6.0 to 6.5 and higher concentrations of ferric chloride than originally used. The HCl injection system and instrumentation were modified to meet this pH range. Control of pH in Reaction Tank 3 was set for 6.4 to assure some margin, as the anionic polymer loses its effectiveness below a pH of 6.0. Because the PPPP WWTS has an arrangement similar to that of Figure 5, this process chemistry was relatively easy to implement. After confirming secondary clarifier performance, the absolute rated cartridge filters were removed from service in February 2008.

- For the primary clarifier, it was determined the sludge was denser at pH 8.6, rather than allowing to operate as high as 9.2. This lower pH reduced the consumption of both hydrated lime and hydrochloric acid. Also, a more continuous transfer of sludge from the clarifier to reaction tank no. 1 was considered to be better, in order to eliminate the interruption of flow from the clarifier during sludge transfer in low WWTS flow conditions such as when only one absorber is online during initial phased startup or during periodic scrubber maintenance or power block downtime.

- Scaling, due to gypsum and ferric-sulfate, occurred in the sand filters, secondary clarifier, and associated piping. The cause of the excessive gypsum scaling in the WWTS is the much higher concentration of sulfate (20,000 to 30,000 ppm) in the absorber slurry and wastewater than originally specified. The cause of this high sulfate concentration is still being investigated, although reactive magnesium in the limestone is one suspected cause. The FGD system was designed for limestone containing up to about 2% $MgCO_3$ of non-reactive magnesium. We Energies is evaluating limestone quality and is considering modifications to Reaction Tank 1 chemistry to reduce the scaling potential of the wastewater and considering an anti-scalant prior to the sand filters. The sand filters were taken out of service in February 2008 because the secondary clarifier effluent was meeting performance requirements for TSS and mercury concentrations. Scale in piping and the secondary clarifier is currently being removed through periodic water flushes and mechanical cleaning.

- Care must be taken for the polymer to be adequately mixed to avoid stratification in the day tank and plugage in the polymer tubing. Regular operator checks and cleaning of the chemical feed equipment is also important, as well as having spare parts immediately on hand.
- The HCl skid was rebuilt with CPVC when the corrosion resistant Hastelloy tubing developed chronic leaks at tube fittings and threaded connections.
- Mercury analysis (EPA Method 245.7 with a minimum detection limit of 1.1 ppt mercury) is performed using cold vapor atomic fluorescence spectroscopy on grab samples collected in specially cleaned 250 ml bottles. Turbidity is used as an indirect indication of mercury, since it was found to correlate well with the formal mercury analysis. Turbidity can more easily be checked and used for control settings. The formal analysis is still performed on the schedule required to report to the Wisconsin Department of Natural Resources.
- One horizontal section of pipe between Reaction Tank 3 and the clarifier flash mix tank was shortened, sloped, and a flush connection added to reduce flow restrictions caused by suspended solids and scaling , which prevented operation at higher flowrates.
- The PPPP FGD alkali-sulfide WWTS has been discharging treated wastewater since November 2007. The system mercury removal performance has been verified up to the design flow rate into Reaction Tank 1 of 94 gpm with mercury concentrations consistently less than 1.0 ppb. Additional tuning of the alkali-sulfide process and evaluation of other enhanced mercury removal technologies will continue at PPPP to minimize future discharges of mercury from the FGD system.

Case Study 2: Wastewater Treatment System for Heavy Metals and Total Nitrogen Reduction

An eastern U.S. 1360 MW (gross) power plant is upgrading to add a LSFO FGD system for operation by 2010 and to produce commercial grade gypsum. Presently, it burns low sulfur compliance coal, typically from Eastern USA. In the future, the power plant will fire a wider range of coals, including low sulfur international coal, mid-high sulfur Eastern coal and possibly other coal types after retrofit of the FGD system. The FGD system will require a chloride purge stream to be discharged from the FGD absorber, via the gypsum dewatering system hydroclones, to maintain absorber chemistry limits. This wastewater will have high concentrations of heavy metals, chloride, biochemical oxygen demand (BOD), phosphate, total suspended solids (TSS) and nitrogen. In order to comply with state standards for water quality, the FGD purge will require treatment prior to discharge.

Additionally, it was determined that an additional periodic blowdown is needed to control the fines concentration in the scrubber when certain limestone is used. The WWTS is designed so the full flow goes first to an equalization tank to attenuate variations in the flow rate and then to a primary flocculating clarifier to remove the fines. About 60% of the flow is then returned to the scrubber and 40% continues through the rest of the wastewater treatment system. The balance of the system is comprised of a transfer tank, two reaction tanks in which the chemicals are added (alkali, organo sulfide, and ferric chloride), a static mixer for polymer addition and the secondary solids contact clarifiers.

The physical chemical treated effluent is then directed to a set of sequencing batch biological reactors. For the flowrate at this plant, three reactors are used to provide parallel operation and adequate redundancy. Associated with the bioreactors are the appropriate pre- and post-equalization tanks. Finally, the treated effluent flows to a set of continuous backwash gravity sand filters for final suspended solids polishing. The final effluent is then discharged.

All solids generated in the primary and secondary clarifiers and the bioreactors are dewatered in a set of filter presses to reduce the amount of water in the solids prior to landfill disposal.

A raw water treatment system was included in the scope of supply to treat secondary treated wastewater from a nearby POTW. The treated water will be fed to the FGD limestone slurry makeup system and will be the source of service water for the FGD wastewater treatment system. The raw water treatment plant will consist of treatment for suspended solids reduction and disinfection. The suspended solids removed in the raw water sand filters are dewatered with the FGD suspended solids.

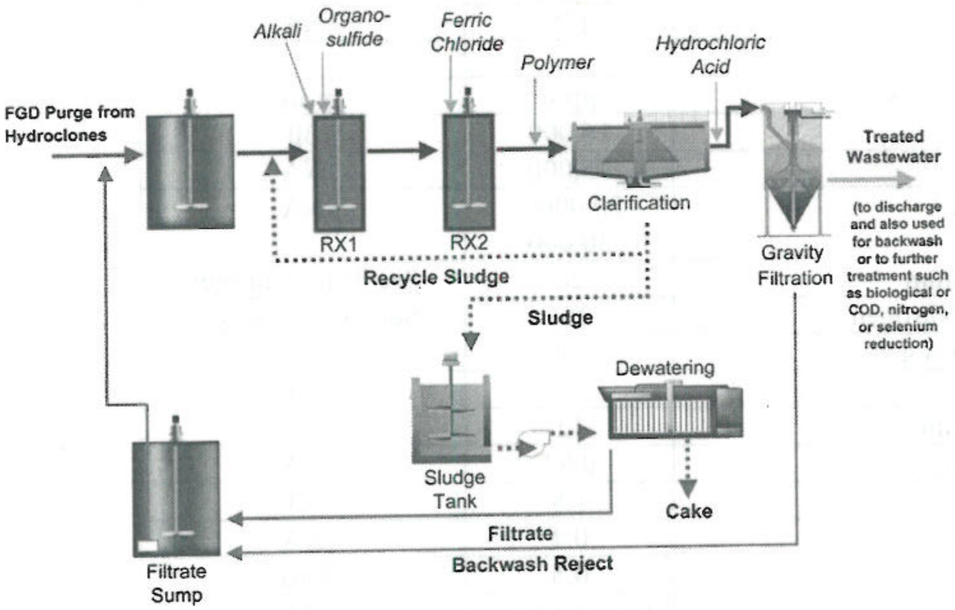
This system is still under construction, thus the lessons learned will be known when start up occurs in late 2009.

Table 4: Characteristics for WWTS with Nitrogen Reduction

Parameter	Specified Purge	Discharge Requirements
pH (S.U.)	4.0 – 6.0	6.0 – 9.0
Temp (°F)	125	NA
Constituents	**ppm**	**ppm**
TSS	16,000	30
TDS	75,000	NA
Chloride	20,000 – 30,000	NA
Ammonium	26	See Total Nitrogen
Nitrate Nitrogen	264	See Total Nitrogen
Total Nitrogen	290	4
BOD	20	20
Aluminum	12	NA
Antimony	0.83	NA
Arsenic	1.8	0.1
Beryllium	0.4	NA
Cadmium	0.5	0.01
Chromium	0.1 (as Cr3+)	0.1
Copper	0.76	0.1
Iron	20	NA
Lead	4	0.1
Magnesium	6,000	NA
Mercury	0.77	0.002
Molybdenum	0.41	NA
Nickel	5(90% particulate)	0.35
Selenium	6.5	NA
Silver	0.3	0.01
Thallium	0.21	NA
Vanadium	1	NA
Zinc	5	0.1

NR – Not reported.
NA – Not applicable, as no discharge limit.

Figure 6: Flow Diagram for WWTS with Nitrogen Removal



Case Study 3: Wastewater Treatment System for Heavy Metals Reduction, Including Special Treatment for Selenium Reduction

A two-unit 1,120 MW coal-fired generating facility in the eastern U. S. was retrofitted with a wet FGD system with two absorbers. The FGD purge stream must be treated for mercury and selenium reduction prior to final discharge to an ash pond and subsequently to a river.

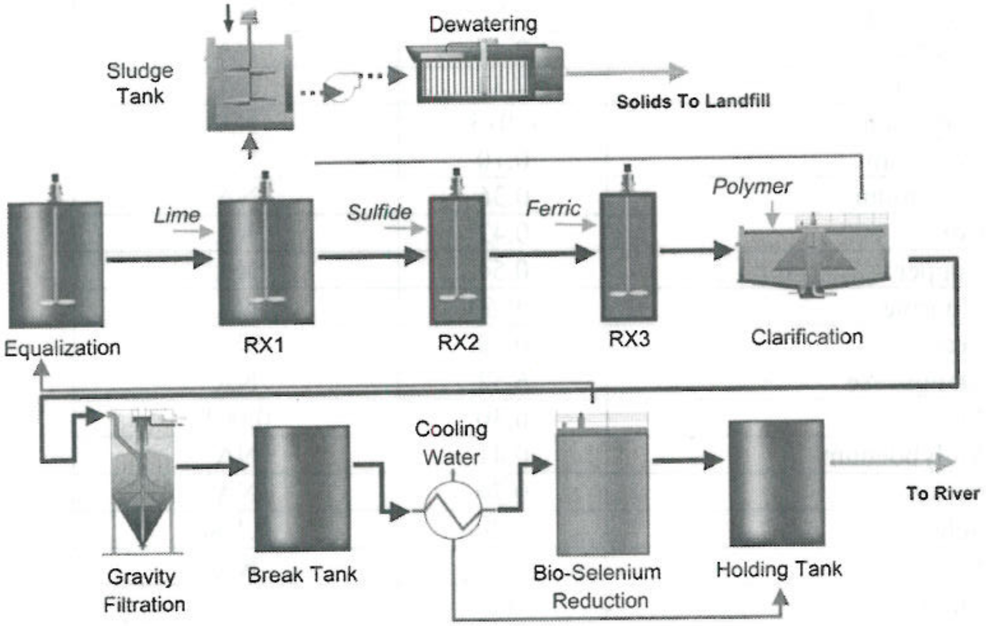
Table 5: Characteristics for Purge Steam Needing Hg & Se Reduction

Parameter	Specified Purge	Discharge Requirements
pH (S.U.)	5.6	5.3 – 9.0
Temp (°F)	124	NA
Constituents	**Ppm**	**ppm**
TSS	16,000	≤50
TDS	25,000	NA
Chloride	12,000	12,100
Ammonium	≤14	NA
Antimony	0.02	NA
Arsenic	0.49	NA
Barium	7.33	NA
Beryllium	0.013	NA
Cadmium	0.10	NA
Chromium	0.36	NA
Cobalt	0.42	NA
Copper	0.54	NA
Fluorine	39.50	NA
Lead	0.35	NA
Manganese	6.52	NA
Mercury	0.30	0.001
Molybdenum	0.41	NA
Nickel	0.76	NA
Selenium	4.0	0.100
Silver	0.06	NA
Thallium	0.2	NA
Vanadium	0.56	NA
Zinc	0.9	NA

NR – Not reported.
NA – Not applicable, as no discharge limit.

Many different treatment technologies and combinations were evaluated before the customer settled on an approach of physical/ chemical and biological treatment combined. The physical/ chemical treatment is for de-supersaturation, pH adjustment, much of the heavy metals reduction (including some selenium reduction), suspended solids removal, and dewatering. Then an anoxic/anaerobic, fixed-film biological treatment system is used for selenium reduction to meet permit requirements. For the bioreactors, activated carbon is used as a support media on which proprietary site-specific naturally-occurring bacteria cultures will grow and be retained within the bioreactor vessels. The microorganisms require a food (carbon) source to support cell growth. A molasses-based nutrient is used and is supplemented with micronutrients proven to promote stable growth for the target microbial population. The dewatering filter presses handle solids from the physical/ chemical and biological processes. The entire system has exceeded expectations and is meeting the discharge requirements.

Figure 7: Wastewater Treatment System with Biological Unit for Mercury and Selenium Reduction



Lessons Learned/Good Engineering Practices for the Physical Chemical, Biological and Sludge Dewatering System

- Selection of appropriate polymer is important for the clarification step. Since polymer effectiveness is not an exacting science, jar testing of similar wastewater can assist in identifying the polymers that could produce the best success.
- Use of potable water in the polymer system at this plant was the correct approach, rather than filtered service water, to prevent the polymer from reacting with compounds in the service water which can increase maintenance activities. Proper mixing of polymer is also essential.
- Drive-through bays on this plant was correct decision for unloading of chemicals and loading of dewatered solids. Not every plant will have adequate space to implement this design item.
- Scrubber units will start up at different intervals; so it is important to have a plan of operation of the WWTS under partial flow conditions, in order to maintain minimum levels in tanks, minimum velocities in pipes, and the chemistry of the treatment process. The chemistry of the FGD purge will likely change during the startups of the FGD units as their operation is adjusted towards optimization.
- Plant staff indicated they would prefer to have all pumps located indoors for access and maintenance.
- Provide large lime prep/storage tank to maintain desired slurry concentrate
- Provide compressed air flushing of polymer lines to ease operator maintenance.
- Provide automatic/programmed flushing of all slurry service lines.

SUMMARY

Proper treatment of the flue gas desulfurization purge stream by a dedicated FGD wastewater treatment system is an essential part of the FGD retrofit project, unless direct or mixed discharges are allowed for a specific power plant, a situation which is uncommon. The required process steps depend on the characterization of the wastewater and the specific requirements of the plant's permit, for both the FGD WWTS discharge and for the combined plant discharge. The system may only require physical-chemical processes, but might also require biological processes, when selenium, nitrogen, or organic compounds must be removed. The selected treatment steps, based on proven process technology, integrated into a system with the appropriate equipment components, controls, operator interfaces, flexibility of design, redundancy of equipment, and good control of the chemistry in the system will result in a reliable operation and ability to meet the plant's discharge requirements.

The design and planned operation of the FGD WWTS must account for the effect of variations in coal composition on purge stream flow rates and composition. The most significant coal variation is the chloride content that, for a given absorber equilibrium chloride concentration, will directly affect the required purge stream flow rate. This flow rate will, in turn, directly affect the concentrations of the other constituents in the purge stream, especially the so-called heavy metals. Differences in composition between Powder River Basin (PRB) and Eastern Bituminous coals can result in notable changes in required purge rates. This impact of coal chloride content is nearly independent of the coal sulfur concentration. For similar reasons, operating the plant with coal of different composition than the design basis coal, can result in purge rates and characterization different than the WWTS design values.

Startup and operation of the latest generation of WWTS has provided "lessons learned", especially with regard to successfully achieving effluent limits for mercury, selenium, and nitrogen, which are more stringent than previous limits. Changes in chemistry may be required to achieve the required effluent concentrations. In addition, because FGD wastewater characterization may be different than the design basis, due to variations in coal and limestone composition, the WWTS operation may have to be adjusted to accommodate unanticipated concentrations of certain dissolved species.

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REFERENCES

1. Cotton, A., Wilkinson, G., Murillo, C., (1999). *Advanced Inorganic Chemistry* (6th Ed.). New York: Wiley.

2. Sonstegard, J., Harwood, J., Pickett, T., *Full Scale Implementation of GE ABMet Biological Technology for the Removal of Selenium from FGD Wastewaters,* International Water Conference, Orlando, 2007.

3. Riffe, M., *Sequential Batch Reactor Treatment for Nitrogen Reduction,* White Paper, 2007.

4. DOE/NETL – 2000/1156, *Milliken Clean Coal Demonstration Project: A DOE Assessment,* Morgantown and Pittsburgh, 2001

5. Mittal, D., Haskin, J., *FGD Blowdown Waste Water Treatment and Zero Liquid Discharge,* International Water Conference, Pittsburgh, 2006.

6. Cleveland, R., Mezo, J., Nickrand, W., Ten Eyck, P., Guidos, J., *FGD Wastewater Disposed of Via Deep-Well Injection at Duke Energy's Gibson Generating Station,* International Water Conference, Orlando, 2007.

7. Eggert, D., Rodgers Jr., J., Hensman, C., *Performance of Pilot-Scale Constructed Wetland Treatment Systems for Flue Gas Desulfurization Waters*, International Water Conference, Orlando, 2007.

8. Murray-Gulde, C., Mooney, D., Huddleston III, G., Rodgers Jr., J., Eggert, D., *Designing Constructed Wetlands for Mitigating Risks from Flue Gas Desulfurization Wastewater,* International Water Conference, Orlando, 2007.

9. Bursik, A., Dieterle, E., *FGD Wastewater Treatment – State of the Art in the Federal Republic of Germany,* International Water Conference, Pittsburgh, 1988.

10. Kutzora, Pete., *FGD Wastewater Treatment using Alkali-Sulfide Process at Pleasant Prairie Power Plant,* Electric Utility Chemistry Workshop, University of Illinois/Champaign, 2008.

Keywords

Flue gas desulfurization, FGD, wastewater treatment, physical chemical treatment, heavy metals, mercury, selenium, nitrogen, biological.