The Thermal ZLD Experience for FGD Wastewater at PSNH's Merrimack Station

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ABSTRACT

Public Services of New Hampshire's Merrimack Station (PSNH) installed a Wet Flue Gas Desulfurization system designed to remove mercury to meet state law requirements. PSNH received notice from EPA that they would not receive an NPDES permit modification in time to support their scrubber installation and startup schedule and that the new final NPDES permit would also not be issued promptly. PSNH had anticipated this risk and proceeded with engineering, procurement, construction and commissioning of a thermal Zero Liquid Discharge System (ZLD) consisting of an evaporator and crystallizers to treat their wet scrubber blowdown stream. The system was unique in that it allowed for both partial and full ZLD operation. This paper will discuss the timeline of events from project identification through commissioning. Lessons learned during commissioning will be presented and discussed.

INTRODUCTION

Coal fired power generation is responding to ever tightening water and air emission regulations and Public Service Company of New Hampshire's (PSNH) Merrimack Station is no exception. The station is located in Bow, New Hampshire and has two cyclone-burner units that total 440 MW net that both burn bituminous coal. Prior to the subject project, both units were retrofitted with supplemental Electrostatic Precipitators for particulate reduction and Selective Catalytic Reactor technology for NOx reduction. The Clean Air Project (CAP) was recently completed to comply with state law (RSA:125-O:11-18) which states "The owner shall install and have operational scrubber technology to control mercury emissions at Merrimack Units 1 and 2 no later than July 1, 2013" (Court, 2006). It further states that the scrubber technology shall be Wet Flue

Gas Desulfurization (FGD) and shall reduce mercury air emissions from coal combustion emissions by 80 percent. The FGD will also provide a reduction of sulfur emissions of over 90 percent.

CAP includes the installation of FGD technology, a physical/chemical wastewater treatment system (Phys-Chem), an Enhanced Mercury and Arsenic Reduction filtration system (EMARS) and a Zero Liquid Discharge system (ZLD). The water permitting process started in 2009 with New Hampshire Department of Environmental Services (NHDES) and PSNH working collaboratively to establish water discharge permit limits for the treated FGD blowdown. The collaboration resulted in the addition of EMARS to the initial, state-of-the-art, Phys-Chem treatment process. NHDES has been the controlling agency and specifies the discharge limits based on water quality standards, with EPA



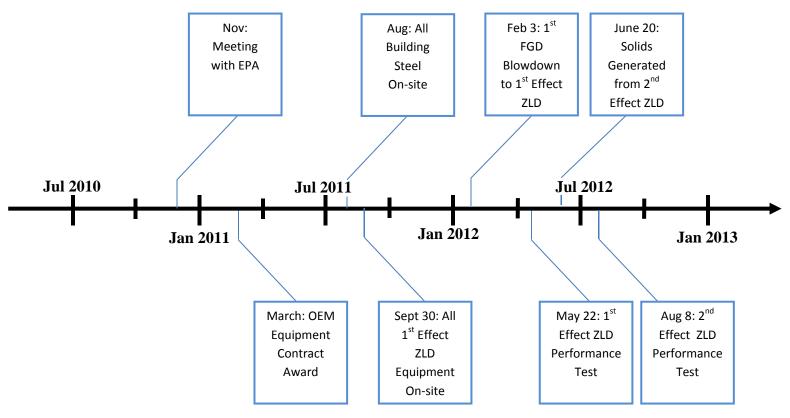


Figure 1 – Project Milestone Dates

typically reviewing and approving NHDES actions.

The agreed-upon plan was presented to the US EPA on November 8, 2010. The EPA, however, believed the appropriate permitting path was to address the new treated FGD discharge in the Station's yet to be issued NPDES permit. The EPA position, requiring any new discharge to be folded into the overall soon to be issued Station Draft NPDES permit, would have resulted in an extended permit process period (many years) due to the statutory requirements regarding public involvement and the unavoidable challenges that a final permit would likely face. A draft of the Station's new NPDES permit was issued by the EPA in the Fall of 2011.

A team of PSNH, Burns and McDonnell, CAP Engineering, Northeast Utilities (PSNH parent company) personnel formed to conceptualize and implement a ZLD solution including design, specifications, procurement, scheduling, installation, commissioning and startup. Competitive equipment proposals were obtained. A release for early engineering and order placement of long lead time materials was made in early January 2011 with a full release to Aquatech in March for the ZLD equipment. Some of the key dates for the project are identified in Figure 1.

PHYS-CHEM EQUIPMENT

The originally procured Phys-Chem wastewater treatment system was

utilized as pretreatment to the new ZLD system. Figure 2 reflects the flow path for the original Phys-Chem system.

This system is located within its own building separate from the power block.

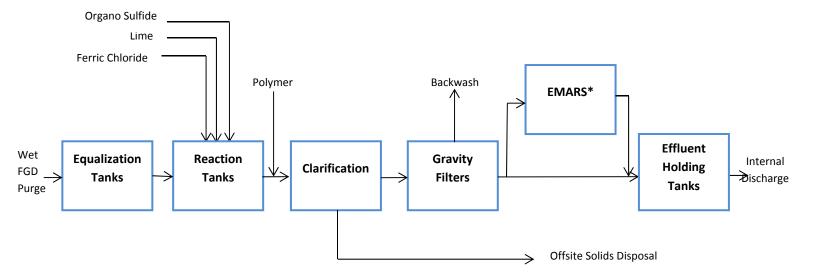
ZLD SYSTEM DESIGN

PSNH sought to reduce risks associated with the NPDES permitting of the new FGD treated effluent and proceeded with engineering and procurement of a thermal ZLD system. Due to the schedule constraints associated with placing the system in service as soon as possible to match wet FGD operation requirements, engineering releases were initiated with multiple equipment suppliers to identify which supplier could meet cost and schedule targets. In March of 2011 the equipment supply

contract was awarded.

DESIGN CHEMISTRY- The system was designed to treat an approximate 65 gallon per minute (gpm) stream of approximately 10,000 parts per million (ppm) chloride wastewater. Table 1 is the design feed chemistry for the First Effect ZLD system.

Influent Water Quality Analysis		
	ppm as	ppm as
	such	CaCO3
Calcium	4,651	11,627
Magnesium	927	3,819
Sodium	200	436
M-Alk	100-300	
Sulfate	1,117	1,162
Chloride	10,000	14,100
Fluoride	118	315
Silica	200	
TSS	< 30	



^{*}Enhanced Mercury and Arsenic Removal System (Siemens)

Figure 2 – Phys-Chem FGD Wastewater Treatment System Flow Path



Table 1 – First Effect ZLD Feed Chemistry

FIRST AND SECOND EFFECT - The initial evaporation scheme (First Effect) was to concentrate the effluent from the physical/chemical treatment system with a vapor compression driven falling film evaporator followed by a steam driven forced circulation evaporator. The concentrated reject stream from the crystallizer would be stored and used as a wetting agent for the fly ash generated onsite and landfilled offsite. The combined distillate produced from the system would be recovered and sent to the wet FGD system as makeup water. See Figure 3 for the process flow.

Modifications were also made to the existing Phys-Chem system. An adjusted pH was required for feed to the evaporator; therefore, the Effluent Holding Tanks were revised from a parallel to a series configuration. The

first tank would have an acceptable pH for EMARS backwash process' and the second tank would have acid feed to reduce pH for the feed stream to the evaporator.

To increase ZLD operational flexibility Second Effect equipment provided the ability to concentrate brine to a dry salt cake. (Generally termed Full ZLD). This operational mode allowed for the mechanical mixing of brine with flyash, brine transport and flyash disposal.

The Second Effect added a multiple effect crystallizer downstream of the original crystallizer for further concentration of the waste stream. Concentration occurs to the point of solubility of the dissolved solids in the stream at which point precipitates are formed and removed from the process with an indexing belt filter. Please see Figure 4 for the Second Effect system flow path.

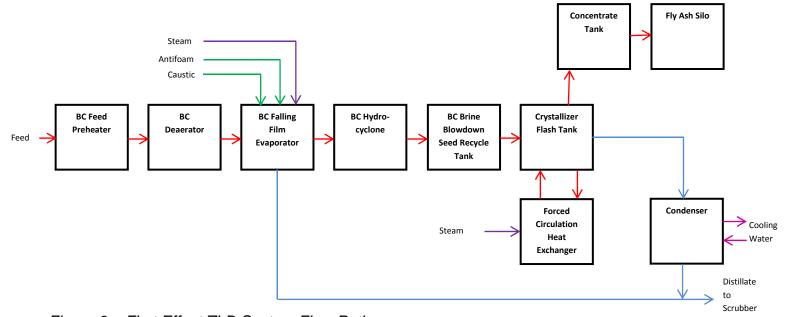


Figure 3 - First Effect ZLD System Flow Path

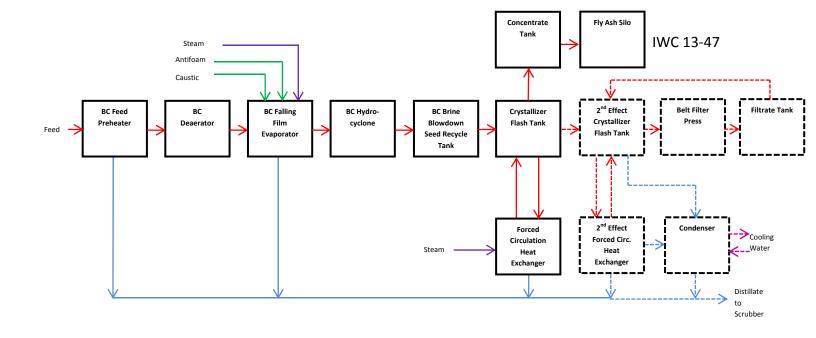


Figure 4 - Second Effect ZLD System Flow Path

The Second Effect included the addition of soda ash to the upstream physical/chemical treatment process to convert the clarifier to a lime/soda ash softener for replacement of the predominantly calcium chloride salts to less soluble sodium chloride salts. The softened chemistry is shown in Table 2 and Figure 3 shows the modified design to include softening requirements.

Influent Water Quality Analysis		
	Unsoftened	Softened
	ppm as	ppm as
	CaCO₃	CaCO₃
Calcium	11,627	1,625-2,113
Magnesium	3,819	997-1,129
		12,208-
Sodium	436	13,516
M-Alk	100-300	
Sulfate	1,162	1,144-1,456
		11,280-
Chloride	14,100	14,100
Fluoride	315	118

Silica	200
TSS	< 30
рН	6.0 to 8.0

Table 2 – Second Effect ZLD Feed Chemistry

SITE CONSTRAINTS – There were multiple site constraints such as a portion of the new ZLD equipment required an indoor installation and space onsite was limited. Discussions centered on the potential to use steam from the main unit as a mechanism for heating the evaporator and crystallizer. But because of distance and cost a small dedicated boiler was provided for the evaporation system in the new ZLD Building.

Because the fly ash silo was located near the generating unit with road access between the unit and the new ZLD building, all piping between the fly ash silo and ZLD building was accomplished using underground

trenching or routed through new or existing buildings.

The wet FGD and Phys-Chem treatment system were under construction during both the design and construction phases of the ZLD system.

Second Effect The ZLD building existing layout was modified to include the Second Effect equipment and operations access within the ZLD building.

As construction of the Second Effect proceeded, First Effect equipment was commissioned and placed into commercial operation. Tie-ins and various construction activities were carefully planned to minimize disruptions to operations.

PROCESS GUARANTEES AND PERFORMANCE TEST RESULTS

As the contracts for the First and Second Effect were awarded sequentially, separate process guarantees and performance tests were required and performed when the systems were completed.

FIRST EFFECT – Maximum concentrate flowrates from both evaporator and crystallizer were specified. These flowrates were based upon the fly ash silo total ash wetting requirements. These flows are predicated upon a minimum treatment rate of 65 gpm of 10,000 ppm chloride feed.

Combined distillate produced from the both the evaporator and crystallizer were guaranteed to be less than 100 mg/L, for non-volatile inorganic total dissolved solids, and have a conductivity of less than 200 micromhos.

SECOND EFFECT – The combined distillate from the evaporator and both crystallizers were guaranteed to meet the same dissolved solids and conductivity limits specified for First

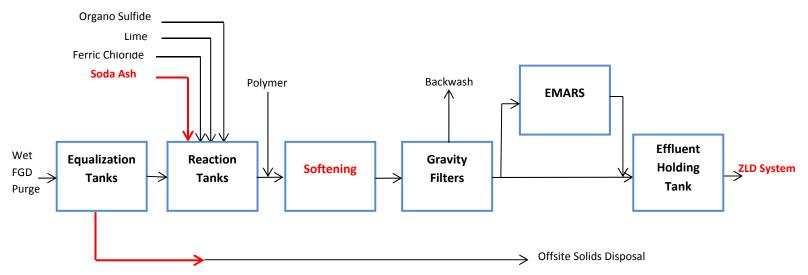


Figure 5 – Modified FGD Wastewater Physical/Chemical Treatment System Flow Path (red indicates changes)

Effect operation. The solids produced in the indexing belt filter were required to pass the EPA paint filter test.

RESULTS – All process guarantees for both the First and Second Effects were met. Distillate quality and minimum treatment rates met or exceeded contractual requirements in all cases.

LESSONS LEARNED

Challenges encountered during the ZLD portion of the CAP commissioning and operation were solved by diligent, ever tightening, plant-wide (coal pile to salt cake) process control. The four areas that most benefited from tighter process control were process pH within the system, salt generation and quantity, Phys-Chem softening and a thorough understanding of the plant water balance.

PH – pH was a process control parameter that required careful monitoring and control from the FGD system through ZLD at every point where it varied. Trace elements in the Phys-Chem feed stream were important to understand and control as upset conditions for these species caused Second Effect chemistry imbalances and operational upsets.

Further, it was very important to understand the quantities of these elements in the fuel and trace them through the FGD, Phys-Chem, and ZLD systems. These elements can greatly affect the pH of various ZLD process streams as well as create compounds in the ZLD system that can agglomerate and cause maintenance and operational upsets.

The pH in the Phys-Chem's second treated effluent tank needed to be controlled to reduce scaling potential in the ZLD equipment. This presented a number of challenges with the Phys-Chem system. Obtaining sufficient mixing within the existing tank also proved challenging.

The ZLD's falling film evaporator experienced significant pH excursions initially. The first instance involved devolving the anti-foam agent into soaplike compound when high values of pH occurred. This situation created "volcanic" foam which permeated all equipment attached to the brine concentrator. The anti-foam agent was replaced with a chemical that was not as sensitive to pH and operations improved.



Elements not properly controlled in the FGD or Phys-Chem also affected pH in the evaporation system. The solution included proper control of the caustic feed and the addition of on-line pH monitoring. The ZLD's crystallizers also evidenced poor pH control that was solved with improved caustic feed and better pH indication.

SALT GENERATION – Salt cake quantity and quality presented many challenges that were solved with tighter process control including, most significantly, a full plant material balance. The incoming fuel constituents, which vary significantly, drastically affected the quantity of salt cake generated. Both the quality and quantity of salt cake greatly affect the throughput of the indexing belt filter. This was solved by generating a plantwide material balance with special

attention to fuel constituents. Picture 2 illustrates high quality salt production.

SOFTENING – A softening process was necessary for Second Effect operation to replace the calcium chloride salts with sodium chloride salts which have a lower solubility than calcium chloride allowing a lower moisture content dry cake. With the original lime feed system in place, a soda ash feed system was added to meet softening needs. Through continued operation the softening process was found to be sensitive to fluctuations and quantities of sulfates within the wet FGD blowdown stream. The following modifications were performed during process optimization.

 The FGD purge hydrocyclones required optimization to reduce variations in sulfate concentrations.

- Modifications were made to the Phys-Chem's upstream Equalization Tank to enhance removal of calcium sulfate solids prior to softening. This tank was modified to function as a settling tank.
- Sludge precipitated in the Equalization Tank is combined with clarification/softening sludge and dewatered with existing Phys-Chem equipment.
- The Reaction Tank feed inlet from the Equalization Tanks was modified to receive only Equalization Tank overflow, filter press filtrate and Phys-Chem building sump contents.

Softening targets played a critical role in the salt cake quality. High calcium

concentrations in the feed to the ZLD (resulting from low soda ash feed) produced very poor salt cake quality. Low levels of calcium (high soda ash feed) led to generation of compounds that agglomerated within the ZLD equipment. Proper process control and process targets solved each of these problems.

WATER BALANCE – For an electric generation station with full ZLD for their FGD waste streams, the water balance required very tight process control and balance. ZLD does not mean "no liquid discharge" rather, all the liquid that is purged from the wet FGD in the blowdown stream must be treated and returned as high quality makeup (in addition to chemical feed dilution water and seal water) to the wet FGD as makeup.

The additional "chemical feed dilution water," was the first target for process optimization. The pumps in both Phys-



Chem and ZLD were converted to closed loop seal system to eliminate unnecessary flush water entering the process and requiring further treatment capacity.

A third step involved using cooled ZLD distillate from the evaporator and crystallizers as the cooling water source for the Second Effect condenser. Not only did this eliminate an additional service water use for the cooling of the crystallizer distillate, the warmed distillate enhances wet FGD operation.

CONCLUSIONS

The Clean Air Project has brought industry leading technology to PSNH's

Merrimack Station. In responding to the NH State Legislature's mandate for mercury reduction at Merrimack Station, air emissions of both mercury and sulfur were reduced with an FGD system and water discharge from the new system was eliminated in a state of the art ZLD facility. The project overcame many challenges through teamwork and close cooperation between the end user, engineer, and equipment supplier, resulting in a highly flexible solution which in essence advanced the technology in a comprehensive systemwide manner.

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