Technical Paper

BR-1944

Salt Drying Technology for Zero Liquid Discharge

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SALT DRYING TECHNOLOGY FOR ZERO LIQUID DISCHARGE

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KEYWORDS: ZLD, Salt Dryer, WFGD, Wastewater, Spray Drying, SDA

ABSTRACT

Due to the recent Effluent Limitations Guidelines (ELG) regulations and local water quality standards being implemented throughout the United States (U.S.), many utilities are searching for the best solution to meet their wastewater treatment needs. Although a range of technologies will be implemented across various facilities, one possible solution is elimination of the wastewater by spray drying. This paper discusses some facilities currently using this technology along with experimental work for wet flue gas desulfurization (FGD) wastewater treatment applications.

INTRODUCTION

On November 3, 2015, the United States Environmental Protection Agency (EPA) promulgated Effluent Limitations Guidelines (ELG) and Standards for the Steam Electric Power Generating Point Source Category. (USEPA, 2015) Included in this rule are maximum discharge limits for flue gas desulfurization (FGD) wastewaters. For existing sources, these limits are summarized in Table 1.

Table 1-ELG Limits for FGD Wastewater for Existing Sources

Pollutant	ELG Limits		
	Daily	Monthly	Long Term Ave
Hg (ng/L)	788	356	159
Se (μg/L)	23	12	7.5
As (μg/L)	11	8	5.98
Nitrate/Nitrate as N (mg/L)	17	4.4	1.3

In addition to these maximum discharge limits, utilities may also have more stringent limits for these pollutants, and limits for additional pollutants, incorporated into their plants National Pollutant Discharge Elimination System (NPDES) permit.

The ELG final rule also includes a Voluntary Incentives Program in which compliance deadlines for existing facilities can be postponed to incentivize facilities to adopt zero liquid discharge (ZLD) technologies which are capable of meeting stricter discharge limits. These discharge limits, which match the limits required for new sources of FGD wastewater, now include total dissolved solids (TDS) and are shown in Table 2.

Table 2 – ELG Limits for FGD Wastewater for New Sources or Existing Sources Enrolling in the Voluntary Incentives Program

Pollutant	ELG Limits		
	Daily	Monthly	Long Term Ave
Hg (ng/L)	39	24	17.8
Se (µg/L)	5	---	5.0
As (µg/L)	4	---	4.0
TDS (mg/L)	50	24	14.9

The limits set forth by the ELG final rule, additional water quality standards based limits, and the extension of compliance deadlines are some of the factors leading many utilities to consider ZLD technologies.

SPRAY DRYING

Spray drying is a process in which a liquid or slurry solution is sprayed into a hot gas stream in the form of a mist of fine droplets. (Geankoplis, 2003) In power generation, spray dryers are most commonly used in spray dryer absorption (SDA) applications in which an alkaline slurry is used to remove acid gases from a flue gas stream. This process is frequently referred to as "dry scrubbing" throughout the industry and a common plant layout is shown in Figure 1.
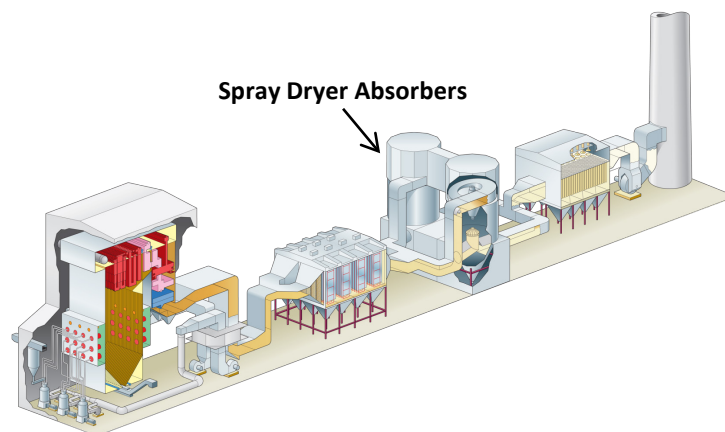

Spray Dryer Absorbers

Figure 1 - Common SDA Plant Layout - shown with Optional Particulate Pre-Collection

Since the initial SDA installation in 1980, SDA has grown to become the most widely used dry scrubbing technology for sulfur dioxide control on utility boilers and can achieve 98% removal for low sulfur coal applications. (The Babcock & Wilcox Company, 2015) AEP Turk, which was awarded POWER's 2013 Plant of the Year Award, is one of B&W's most recent SDA installations and demonstrates the success of spray dryers in this industry. (Peltier, 2013)

Spray drying applications extend well beyond power generation and include the production of laundry detergents, pharmaceuticals, plastics, pigments, instant coffee, powdered milk, and many more. (Masters, 1985) Another spray drying application is salt drying. In salt drying applications, a liquid or slurry containing a significant concentration of dissolved salts is dried in a hot gas stream. During the drying process, as water is evaporated, the dissolved salts concentrate in solution. As the solubility limit of each salt is reached, the salt precipitates and becomes part of the total suspended solids (TSS). This process continues until nearly all of the water has evaporated and the previously dissolved salts are now all suspended solids entrained in a gas stream. Separation of the dried salts from the gas stream can be accomplished with common particulate control devices such as pulse jet fabric filters (PJFF) and electrostatic precipitators (ESP).

Salt dryers have been used to treat wastewater from wet FGD systems in the waste incineration industry since the early 1980s. GEA Niro, B&W's partner in spray drying, has installed over 25 salt dryers worldwide, three of which B&W recently visited to review operation and engage in technical discussions. Some of the key operating data from these visits is shown in Table 3 which also includes data from Nordjyllandsvaerket unit 3 (NJV3), a coal fired facility located in northern Denmark. (Knudsen, 2006)

Table 3 - Nominal Operating Data from Existing Salt Dryers

Plant	Spray Chamber Diameter ft	Outlet Temperature F	WFGD Effluent Flow gpm	Chlorides ppm	pH	TSS wt%
Plant A	28	345	11.5	70000	6.2	3.5
Plant B	33	350	18.5	70000	6.2	6
Plant C	33	325	22	52000	7	4.5
NJV3	26	285	26.5	30000	?	?

A common layout of a waste-to-energy (WTE) facility using a salt dryer for ZLD is shown in Figure 2. (MartinGmbH) Moving from left to right on the diagram is waste handling followed by the furnace and convection path, denitrification, salt drying, carbon injection, particulate control, and two stage wet FGD. Although Figure 2 represents a typical system, variations do exist from plant to plant.
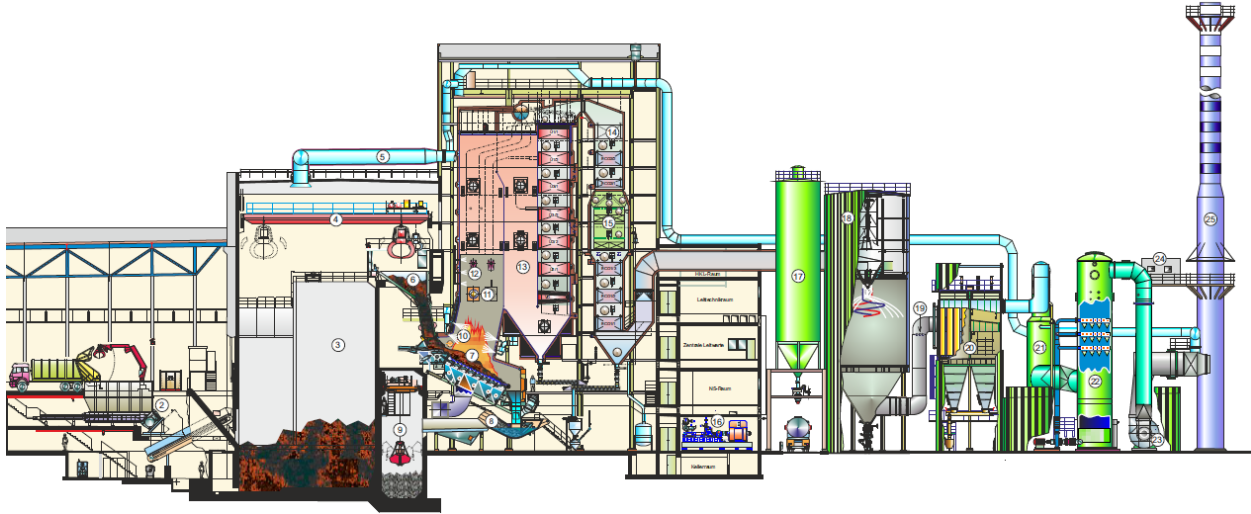
Figure 2 - A Common Layout of a Waste to Energy Plant using a Salt Dryer for ZLD

One of these variations is in the particulate control technology of each plant. The older plants tended to use ESP for particulate control while the newer plants usually had PJFF; one plant with both old and new units, used both ESP and PJFF.

In addition, the material handling systems for the salt dryer byproduct varied from plant to plant. One plant used pneumatic conveying, another had screw conveyors, and the last plant used drag chain conveyors. Because the byproduct is predominantly calcium chloride, which is hygroscopic and can pull moisture from the surrounding air thereby transitioning from a solid to a liquid, all of these systems had precautions in place to prevent this. In the pneumatic system, the conveying air was very dry eliminating the ability of the salts to absorb moisture even at reduced temperature. The screw and drag chain conveyor type systems were entirely enclosed and had heat tracing in place to maintain a high enough temperature to prevent deliquescence of the salts.

The wet FGD systems at these plants used dual stage scrubbers in which the first stage captures the majority of the HCl and the second stage captures the majority of the SO_2. Unlike in the U.S., where dolomitic limestones are often used as the reagent for wet FGD, two of these plants used higher quality lime as the reagent. The third plant operated a dual alkali system in which NaOH is used in the scrubber and the scrubber liquor is sent to a separate system where hydrated lime is added thereby precipitating gypsum and calcite while regenerating the NaOH reagent for recycle. The gypsum and calcite slurry is mixed with the high chloride purge stream from the first scrubber stage before being supplied to the salt dryer.

In general, maintenance was reasonable across all of the facilities. Overall operators were content with the performance of their salt dryers and claimed that issues with other equipment at their facilities were much more common. The plants reported that usually the salt dryers only have issues during shutdown periods when residual salts are left in the system and the equipment is allowed to cool to temperatures at which moisture can be pulled from the surrounding gas.

Although the major equipment is the same, there are differences between salt dryers in WTE applications and those applied to coal-based power generation in the U.S. Because flue gas

temperatures differ, the salt dryer will likely be placed in a slipstream instead of in the full flue gas stream for coal applications as shown in Figure 3. The slipstream design helps ensure that the salts are dried properly to avoid material handling issues and also prevents the need for a much larger spray chamber or multiple spray chambers to evaporating effluent in the entire flue gas stream.

In addition, Figure 3 shows some of the options for collection of particulate exiting the salt dryer which includes the dried salts and flyash. Although the addition of a separate particulate control device on the slipstream increase capital costs and adds pressure drop, this prevents contamination of the flyash collected in the existing ESP or PJFF.
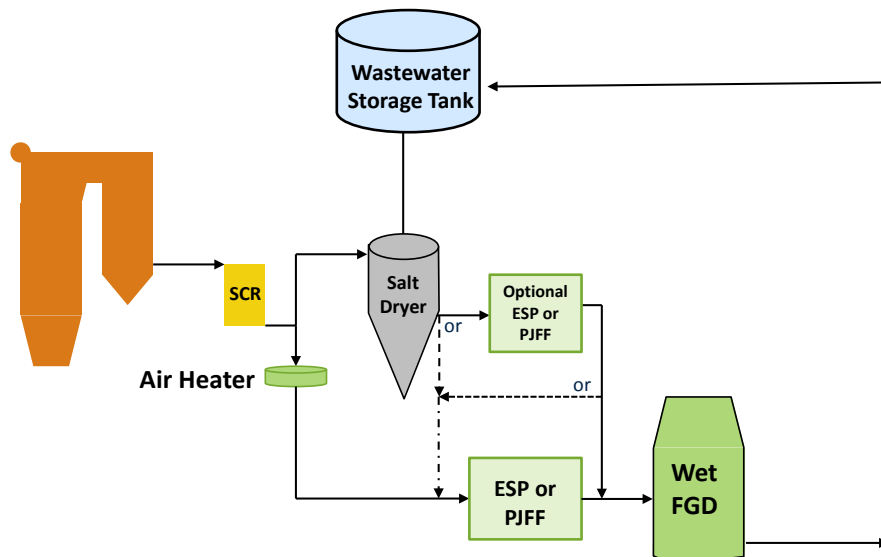
Figure 3 – Common Salt Dryer Process Flow Diagram

TECHNICAL STUDIES

As part of extending the salt dryer technology from WTE applications to U.S. coal fired wet FGD evaporation, several technical studies were carried out. These studies included modeling simulations, pilot testing, and lab scale testing which each investigated various aspects of salt drying.

PILOT TESTING – Located at the Babcock & Wilcox Research Center is a 6 MBtu/hr pilot small boiler simulator (SBS). This facility includes nearly all environmental technologies found in U.S. coal-fired utilities and was designed to allow for a wide range of pilot tests. (See Figure 4.) One of the systems that is part of the SBS facility is a spray dryer which was used for salt dryer pilot testing.
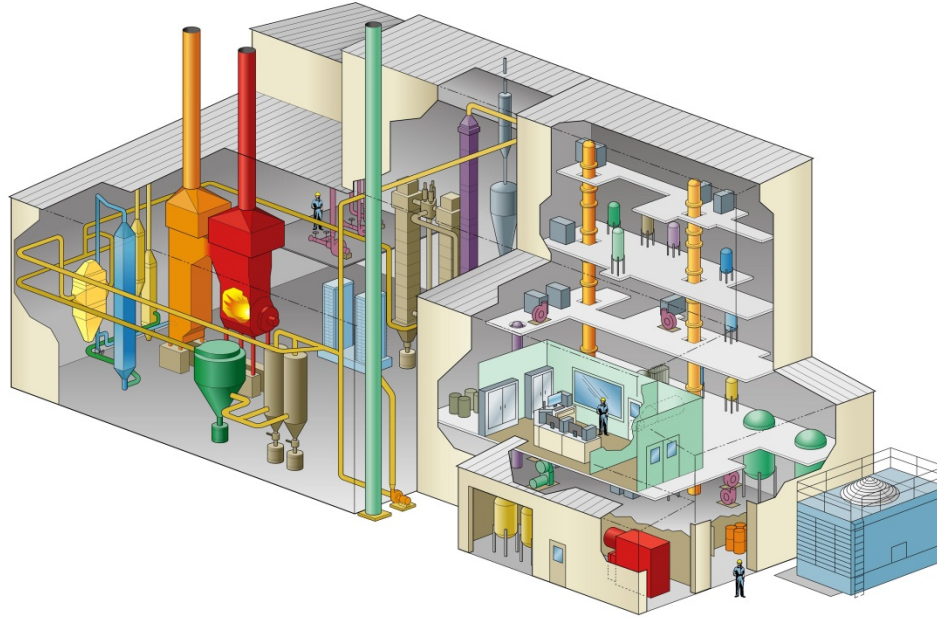
Figure 4 - Babcock & Wilcox Research Center Pilot Facilities

For the pilot test, FGD effluent from a utility burning eastern bituminous fuel was obtained. Due to the highly variable nature of FGD wastewater, the compositions of the slurries sent to the atomizer during different test conditions were modified with various additives. The ability to adjust the composition of the atomizer feed allowed investigation of the impacts of constituents and concentrations in the wastewater on the drying process. Some of the constituents in which the concentrations in the wastewater were changed include total suspended solids, total dissolved solids, chlorides, bromides, sulfates, magnesium, and the pH.

In addition to the investigations on the impacts of the wastewater composition, other process variables were investigated. These included changes to the flue gas inlet and outlet temperatures, the flue gas composition, spray chamber residence time, and rotational speed of the atomizer. Unlike most utilities using rotary atomizers, the pilot-scale spray dryer used in these tests included a variable frequency drive to change the atomizer speed. The speed of the atomizer is very important as it is tied directly to the droplet size distribution of the atomized slurry with a higher atomizer speed corresponding to smaller droplet sizes. Although most test conditions were carried out at atomizer speeds which would be representative of utility-scale atomizers, some tests were run at much lower atomizer speeds to investigate drying rates of larger droplets.

During the pilot testing, data was collected in several ways. One primary source of information was the dried salts generated during the test. The dried salts, after exiting the spray chamber, were collected in a PJFF. During the test, the PJFF was set with a high pulse frequency to minimize the amount of additional salt drying that took place on the bags. The dried salts were then collected in hoppers and transferred into drums where samples could be taken and sent for

analysis. The primary analysis used to quantify how well the salts dried during the test condition was a loss in weight measurement in which residual water is driven off using a heat source.

Another source of data came through temperature profiling of the spray chamber. The pilot scale spray chamber includes chains which hang along the circumference of the spray chamber. Along the height of each chain, thermocouples are positioned to take temperature measurements during operation. This system, which included over 300 thermocouples, was run continuously during the pilot test and generated data that could be correlated with good drying as shown in Figure 5 and poor drying as shown in Figure 6.
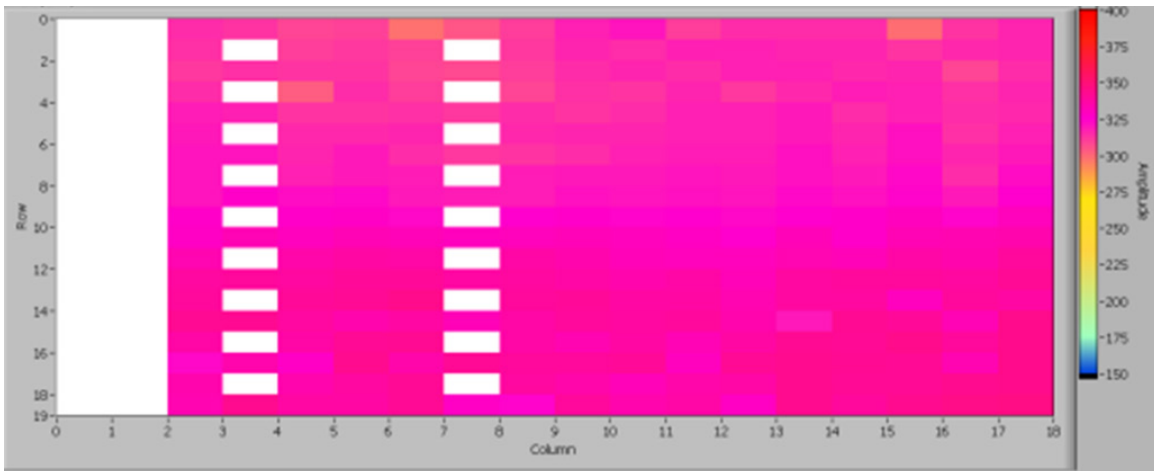
Figure 5 - Example of Process Condition with Good Drying
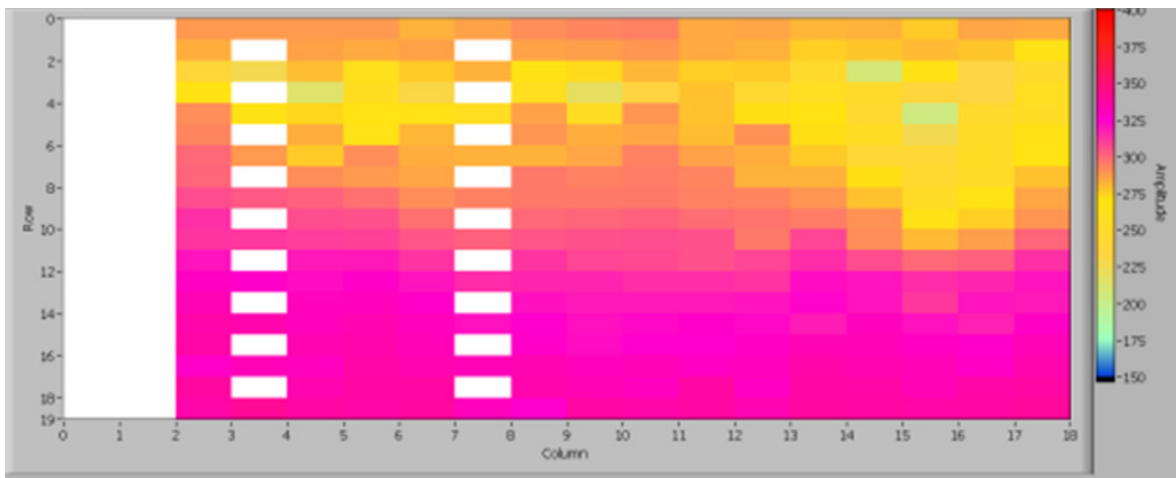
Figure 6 - Example of Process Condition with Poor Drying

In addition to the measurements made for the determination of drying rates, the flue gas composition was also continuously monitored for various constituents using Fourier Transform Infrared spectroscopy.

MATERIAL HANDLING TESTING – Aside from the data collected during the pilot test, additional information was gained from the generation of salt dryer byproduct under a wide range of conditions. In addition to the extensive chemical analyses that were performed, critical properties required for the design of material handling systems were also measured. An example of material handling information collected is shown in Figure 7. Material handling properties were measured for multiple dried salt samples. This allows incorporation of favorable salt dryer operating conditions into future commercial salt dryer designs to improve material handling systems and reduce the risk of potential material handling issues.
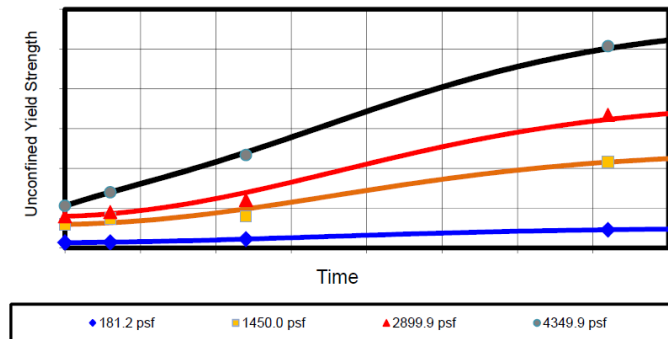
Figure 7 - Unconfined Yield Strength as a Function of Storage Time

In addition, scanning electron microscope images were taken which show the salt dryer byproducts under high levels of magnification. (See Figure 8.)
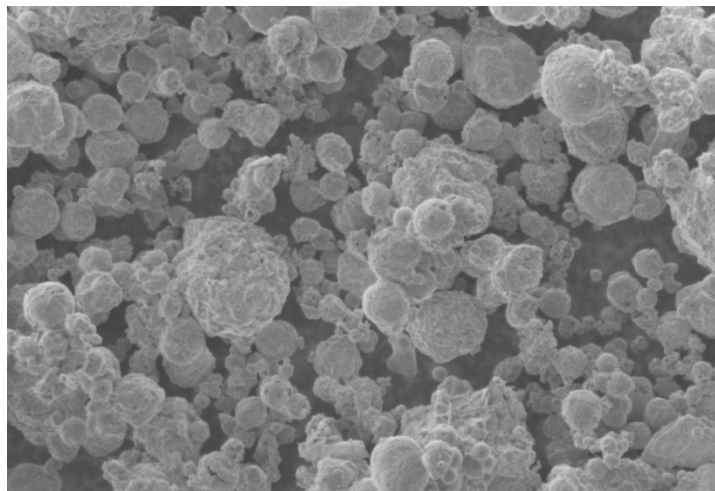

Figure 8 - SEM Photograph of Salt Dryer Byproduct at 1000x Magnification

CORROSION TESTING – Although there were no reports of noticeable corrosion from any of the existing salt dryers in WTE applications, corrosion testing was done using the salt dryer byproducts from the pilot test due to the presence of chlorides. These tests were carried out in an advanced fireside corrosion laboratory at B&W's research center. This laboratory is typically used to investigate the performance of emerging and existing materials for upcoming power generation applications over a very broad range of simulated environments, temperatures, and extended periods of over 1000 hours.

The fireside laboratory includes an enclosed Lindbergh tube furnace equipped with a quartz process tube with the capability to operate at an accurately controlled temperature. Preheated synthetic flue gas is supplied to the furnace to expose test specimens to nearly any environment typically encountered during combustion or in the flue gas path. Test coupons, exposed to a surface deposit, are then placed into the furnace and brought up to test temperature. The composition of the flue gas is precisely controlled by means of calibrated mass flow controllers designed for the specific gases and flow rate requirements. A photograph of the test set-up is shown in Figure 9.

Figure 9 - Corrosion Test Set-Up

For the salt dryer testing, two different metallurgical compositions were exposed to the salt dryer byproduct: carbon steel A36 (ASTM A36, UNS K02600) and Corten-A (ASTM A242, UNS K11510). Test specimens included base metal coupons of A36 and Corten-A, and welded coupons of Corten-A. The tests were run for up to 1000 hours under representative process flue gas compositions and temperatures.

Results from one of the corrosion tests are shown in Figure 10. Because the measured corrosion rates were less than 2 mils per year (mpy), the corrosion resistance of these materials has been classified as excellent according to general industry standards for the conditions tested. It should be pointed out that corrosion rates are expected to increase if the temperature is below the deliquescence point, which depends on the moisture of the surrounding air, of the salt dryer byproduct sample allowing the material surface chemistry to change from solid-metal to liquid-metal.
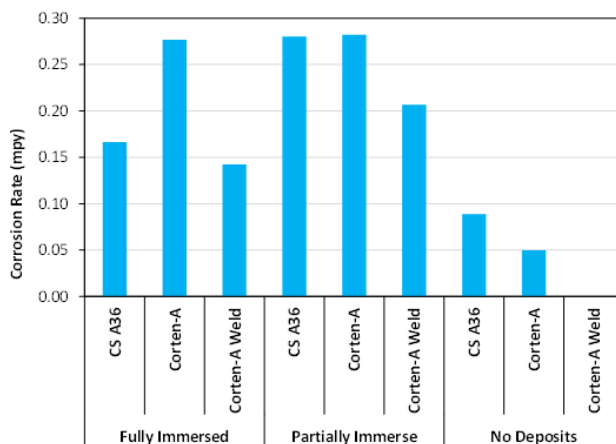
Figure 10 - Corrosion Rates with Exposure to Salt Dryer Byproduct

VOLATILIZATION TESTING – The intent of salt drying is to evaporate water and to collect all of the dried salts as solids. Volatilization of species which would allow them to slip through the particulate control device is undesirable. Testing was done to 1) identify constituents in the wastewater that could volatilize and 2) investigate methods to mitigate unwanted species evaporation.

A laboratory-scale test facility was designed, built and operated to evaporate and subsequently condense various wastewaters under different conditions. The evaporated wastewater was cooled to around 34F to condense any volatile species that were also evaporated from the wastewater. The wastewater was sampled before a test and the residual wastewater and condensate were sampled throughout various extents of the evaporation test. Finally, the condensate was sampled after almost all of the wastewater had evaporated. The wastewater samples were then filtered to separate the liquid and the solid portions and all samples were analyzed for total suspended solids and concentration. The concentration was determined by chemical fractionation of over 30 elements using inductively coupled plasma mass spectrometry.

A mass balance was then performed at each evaporation extent throughout the experiment to determine how much of each element was present in the wastewater solids, in the wastewater liquid, and in the condensate. The fraction collected in the condensate would therefore mostly represent the material that had volatilized during evaporation.

Charts were generated based on the results for each element. The charts are presented with the percentage of the initial water that had been evaporated up to that point, referred to as the evaporation extent, on the X-axis. The chart format allows visual observation of the evaporative process for each element.

Example charts are shown in Figure 11 for selenium and mercury. As can be seen from the selenium chart, initially around 89% of the selenium in the wastewater is present as part of the suspended solids while the remaining 11% is dissolved in the liquid. As evaporation begins, more of the selenium becomes dissolved due in part to the elevated temperature. As evaporation continues the concentration of selenium in solution will increase. Between 55% and 69% evaporation extent, selenium salts begin to precipitate and are present as part of the suspended solids in the wastewater. This trend continues upward until the final measurement at an

evaporation extent over 86% in which over 94% of the selenium is present in the wastewater solids. Around 5% of the selenium is still present as a dissolved constituent while 0.16% of the initial selenium ended up in the condensate. Mercury is known to be a more volatile metal, so as expected, significantly more mercury volatilized than selenium.
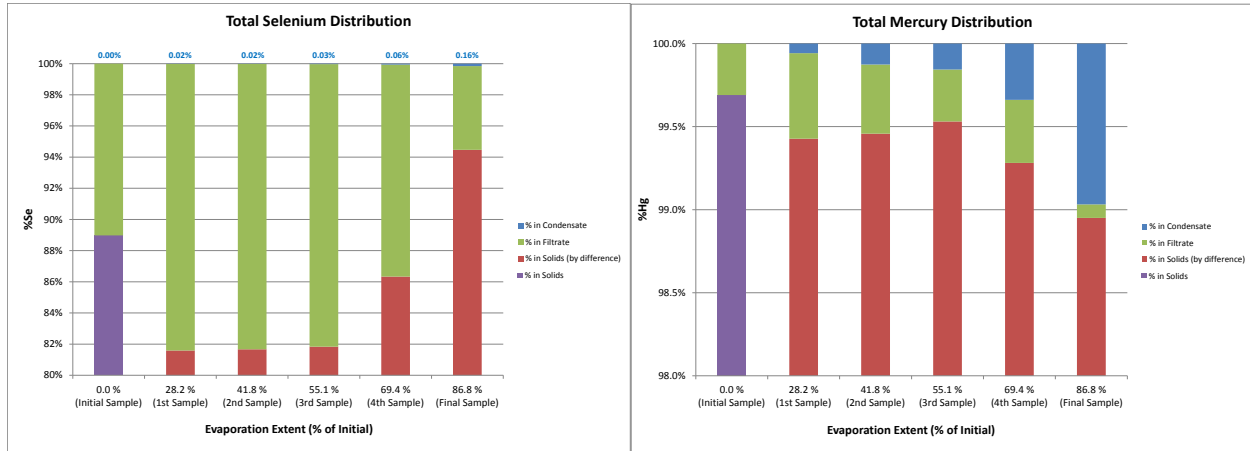

Figure 11 - Example Charts from Volatilization Testing for Se and Hg

The above charts for selenium and mercury only represent a single test for a specific wastewater. Many other tests were carried out to look at various wastewaters, evaporative conditions, and additives that could be used to reduce volatilization. Included in this were speciation studies that looked at the various forms that elements can be present as such as selenite and selenate.

CONCLUSIONS

Spray drying is a mature technology that was developed over a century ago and is a technology that has existed in the US coal fired power generation industry for over 30 years to remove SO_2 from flue gas. In the waste to energy industry, salt dryers are used to treat similar wet FGD effluent to prevent the discharge of wastewater from many plants in the industry.

The salt drying technology is expected to transfer into the U.S. coal-fired power generation industry for treatment of FGD wastewater in part due to its success in similar applications. A lot of additional technical studies have been done to supplement the existing salt dryer experience and ensure this technology can be implemented successfully. All of this work and experience has led to several B&W salt dryer commercial project evaluations and commercial offerings which can be summarized in Table 4.

Table 4 - Recent Utility Salt Dryer Project Evaluations

Unit Size	Coal Cl	Wastewater Properties		Flue Gas Properties			Spray Chamber Diameter	Plant Impacts	
		Flow Rate	Chlorides	Inlet Temperature	Outlet Temperature	Flow Rate		Parasitic Load	Boiler Efficiency Loss
Gross MW	% by Weight AR	gpm	ppm	°F	°F	% of Total	ft	%	%
~1400	0.11%	150	40,000	650	330	NA	49	0.08%	Not Calculated
~725	0.12%	110	20,000	650	330	11.5%	46	0.19%	0.21%
~900	Not Provided	200	21,000	650	330	12.5%	52.5	0.12%	0.30%
~550	Not Provided	80	50,000	710	330	8.5%	37	0.05%	Not Calculated

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