Technical Paper

BR-1940

Wet FGD Effluent Characterization in Preparation for WWT Technology Selection

Authors:
T.R. Parsons
S.R. Brown
R.F. DeVault
J.P. Chenevey

Babcock & Wilcox
Barberton, Ohio, U.S.A.

Presented to:
Power Plant Pollutant Control and Carbon Management "MEGA" Symposium

Date:
August 16-19, 2016

Location:
Baltimore, Maryland, U.S.A.

Babcock & Wilcox

Wet FGD Effluent Characterization in Preparation for WWT Technology Selection

Paper # 26
Presented at the
Power Plant Pollutant Control and Carbon Management "MEGA" Symposium
August 16-19, 2016
Baltimore, MD

Ted R. Parsons, Shannon R. Brown, Richard F. DeVault, and Justin P. Chenevey, The Babcock & Wilcox Company (B&W), Barberton, OH

ABSTRACT

Characterization of effluent from wet flue gas desulfurization (FGD) units serves as a critical basis for engineering decisions regarding which waste water treatment (WWT) technology options are best suited to meet a plant's specific requirements, and for understanding the advantages and risks associated with each solution. With the Effluent Limitations Guidelines (ELG) revision of 2015, utilities with wet FGD units have cause to review the chemistry of the wet FGD blowdown. Such undertaking can be difficult due to changes in coal composition, swing load operation, and individual unit operating parameters. Wet FGD blowdown chemistry can vary between units, and has been observed to fluctuate significantly over time for the same unit. This paper will discuss measurement methods, data collection type and frequency, considerations for data integrity and analysis, and overall system implications for characterization of wet FGD effluent in preparation for WWT system selection.

INTRODUCTION

Strategy development and execution is underway by steam electric generating utilities to meet a new wave of environmental regulations. Coal-fired electric generating units serve to provide consistent electric power safely, consistently, and within regulatory compliance. In 2015, the US EPA issued revisions to the federal Effluent Limitation Guidelines (ELG) and Standards for the Steam Electric Power Generating Point Source Category. These guidelines provided new limitations for the composition of waste water from wet Flue Gas Desulfurization units treating flue gas, prior to discharge at an outfall or reuse within the power plant [1]. The revised EPA guidelines for wet FGD waste water are summarized in Table 1. The new, tighter limits on arsenic, mercury, selenium, nitrates/nitrites have put more rigorous demands on wet FGD Waste Water Treatment Systems. These guidelines will need to be implemented as plants renew their national pollutant discharge elimination system (NPDES) permits; generally, plants continuing to discharge waste water at an outfall will be expected to be in compliance between 2018 and 2023 [2]. Adding complexity to compliance strategies, states and local regulatory bodies may impose more stringent requirements on effluent quality discharging to a specific body of water or watershed. For example, discharge into the Great Lakes, the Mississippi River, protected natural areas, or into public-use waters may require a more stringent water quality for discharged effluent than required by federal guidelines [3]. Local authorities have broad discretion over waters within their jurisdiction and are involved when discharge permits are renewed.

Table 1. EPA Steam Electric Power Generating Effluent Guidelines for Wet FGD Waste Water [1].

	Existing Sources			New Sources & Voluntary Program for Existing Sources		
	Long-Term Average	30-Day Average	Daily Maximum	Long-Term Average	30-Day Average	Daily Maximum
Total Arsenic [μg/L]	5.98	8	11	4.0	a	4[a]
Total Mercury [ng/L]	159	356	788	17.8	24	39
Total Selenium [μg/L]	7.5	12	23	5.0	a	5[a]
Total Nitrate-Nitrite as N [mg/L]	1.3	4.4	17			
Total Dissolved Solids [mg/L]				14.9	24	50

a – For mercury and selenium, the daily maximum limitation is set at the quantification limit. The monthly average limitation is not established when the daily maximum limitation is set at the quantification limit, per the standard.

With a timeline of 2-7 years for most sites to be ELG compliant, and a typical 2 year time requirement for engineering, procurement, construction, and commissioning of major projects, utilities have a short timeline in which to select any new or changed WWT technologies that their systems may require. With matters of regulatory compliance, it is likely that only demonstrated technologies will be considered. If a demonstration on a specific wastewater is required, more time will be needed in the implementation schedule. For those voluntarily selecting what is known in the industry as a zero liquid discharge (ZLD) approach, there is a possible extension in the compliance timeline but, in either case, time is short considering the amount of work required for implementation. Thus, there is an urgency for system owners who have not already selected a WWT technology to make a decision and move forward.

Information from a wet FGD waste water characterization program can be instrumental in developing a design basis for new WWT technologies. Historical data is particularly valuable if it can capture variations in wastewater properties over a range of expected fuels and operating conditions. Providing this information to a WWT system supplier gives a more complete picture of what the system will have to treat, and maximizes the chance of a successful application of the technology. Given the tight timeframe for ELG compliance, moving forward with a technology that is unsuitable for the range of operating conditions it will encounter, or one which requires significant re-engineering and rework in order to succeed, are situations to be strenuously avoided.

Variability and Fluctuations – Do You Know Your System?

Wastewater from wet FGD systems is one of the more challenging waste streams to treat, not because of toxicity, but because of variability. The composition and properties of this wastewater is a function of the upstream chemistry in the wet FGD absorber. The chemistry in the wet FGD absorber is itself a function of the composition of the fuel being burned, the reactivity of the SCR catalyst, the carryover of ash, ammonia, and ozone from upstream equipment, and of different additives which may be added to the coal, injected upstream of the wet FGD absorber, or added to the absorber itself [4]. Absorber chemistry is also affected by limestone composition and reactivity, make-up water composition, and by the boiler load. Finally, some of the chemical reactions between species are slow kinetically, and compositions can change during the time that the slurry passes through the absorber, is filtered, and passes out to the wastewater treatment unit [5]. To compound the challenge, many of the factors change regularly (*e.g.* boiler load, fuel composition, upstream unit operating parameters, seasonal variation of make-up water, start-ups, shutdowns), so absorber chemistry is rarely in a constant, steady-state condition. Absorber chemistry typically varies from plant to plant, and has even been known to vary between wet FGD absorbers at the same plant [6]. This degree of variability coupled with extremely low discharge limits for regulated constituents makes this a complex and difficult waste water to treat.

Changes in absorber chemistry and operation may make themselves felt in the WWT system as oxidation reduction potential (ORP) excursions, higher ash fines concentrations, increased trace metals concentrations and changes to chemical speciation, among other effects [7]. Many of these can have a detrimental effect on the performance of the WWT system. ORP excursions can cause upsets in biological treatment units, and fluctuating inlet concentrations can lead to problems meeting outlet concentration limits. Partitioning of dissolved metals into more soluble species (e.g. selenate instead of selenite, arsenate instead of arsenite) can reduce the ability of traditional chemical physical treatment systems to adequately remove these metals. The presence of higher concentrations of bromine or iodine from mercury control additives may cause gas evolution in evaporative crystallizers. Being able to characterize the wet FGD wastewater and define the variation within reasonable bounds will facilitate the selection of the best technology for addressing ELG for a particular plant.

PROJECT APPROACH

A wastewater characterization plan to develop data for technology selection is best individualized for each site. There are a number of factors to consider in its design. On the fuel side, the frequency of changing fuels is a major factor that should drive the frequency of sampling and testing. When a low sulfur or low chloride coal is burned, the "chlorides" purge rate from the wet FGD system is low when the design chlorides level is held. The low purge rate results in higher concentrations of dissolved metals, dissolved salts, inerts, and fines. The amount of sulfur in the fuel also affects ESP operation. Higher sulfur fuel results in lower ash resistivity which creates greater spark rates. Precipitator operation is thought to be strongly related to the presence of strong oxidizers and high ORP levels in wet FGD absorbers [4]. The more frequently the fuels change, the more extensive the monitoring and sampling program should be to capture the effects on wastewater. Other factors that have a significant effect on wastewater chemistry are the frequency of load cycling, electrostatic precipitator (ESP) excursions, change of limestone, and the use of additives. Sampling around these events is recommended, as is around any apparent ORP excursions. The key is to focus on sustained changes and ignore momentary "spikes" that make up the usual operating "noise".

The measurements needed to characterize wet FGD wastewater will come from measurements already being taken to monitor wet FGD operation, from grab samples taken at the wet FGD secondary hydroclone overflow, and at the outlet of the existing wastewater system. The stream from the secondary hydroclone overflow is usually the wet FGD purge stream. If the system does not have a secondary hydroclone, then sample the feed from the wet FGD system to the WWT System. Readings from in-line monitors for absorber pH, ORP, and temperature can be tracked in real time through the DCS historian. The collection of grab samples may need to be timed to correspond with excursions shown by in-line measurements, depending on where the absorber is in the bleed cycle (wet FGD absorbers typically operate in a semi-batch mode and may not be dewatering when continuous monitoring indicates an event of interest).

The grab samples should be tested for pH, ORP, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), cations (especially calcium, magnesium, arsenic and selenium), anions (especially nitrates, nitrites, and chlorides), and mercury. Mercury is called out separately because the extremely low regulatory limits require specialized testing and handling procedures to prevent contamination and to get meaningful readings at such low levels. The described tests should result in an adequately defined profile of the waste water.

A good wastewater characterization program will include continuous measurement of pH and ORP of the absorber slurry by in-line probes. It is therefore important to have a good probe maintenance program to ensure that they are reporting reliable data. This is particularly important with the pH probes because of the logarithmic nature of the pH scale, where a difference of 0.5 pH units corresponds roughly to a factor of three. A good guideline is to check the calibration of the probes once every three days, or whenever multiple probes' readings differ from each other by more than 0.25 pH units. The probes should be removed from the process and run through a three-point calibration for pH, where they would be checked against three standardized buffer solutions. A two-point calibration may be performed for the ORP probe using standard ORP buffer solutions. If any of the probes is shown to be out of calibration, it should be cleaned per the manufacturer's instructions and retested. If it cannot be brought into proper calibration, it should be replaced. This should already be part of the routine maintenance program for the wet FGD system, so this should not require additional effort on the part of the plant.

Four sets of grab samples should be taken for the wet FGD purge outlet and the wastewater system outlet at each sample interval. The pH, ORP, and temperature readings at the time of sampling should be measured using portable meters and recorded. The first set of samples should be tested for TSS and TDS as soon as practical, since there is interaction between the liquid and solids until full equilibrium is reached. The pH, ORP, and temperature of the samples should be measured and recorded at the time of analysis, also. The second set should be tested for trace metal cations, the third for anions, and the fourth set tested for mercury. There is much more cleaning rigor required for the sample bottles and sample equipment being used for trace metals and anions testing. The low concentrations being measured makes the testing highly susceptible to contamination, so scrupulous sampling and lab technique must be employed. The regulatory limits for mercury are orders of magnitude lower than the trace metals, so mercury testing is even more susceptible to contamination, and more rigorous sampling and laboratory techniques must be employed. The cations and anions samples and mercury samples should be filtered just after collection. The cations sample needs to be preserved with nitric acid and the mercury sample needs to be preserved with hydrochloric acid just after collection. Both acids need to be of trace metal grade quality.

There are a number of approved test methods that can be used to determine trace metals, nitrates, and mercury. EPA approved test methods may be accessed from www.epa.gov/cwa-methods. There is also a table in the Federal Register that cross-references approved test methods for different constituents with available analytical instrumentation [8]. The test methods themselves go into great detail about equipment preparation, sample collection, preservation of samples, test procedure, interferences, and allowable holding time before analysis.

An applicable test method for cations is EPA Method SW-846-6020B [9]. This method uses inductive coupled plasma mass spectroscopy to detect concentrations of 23 metals of interest including calcium, magnesium, arsenic, selenium, and thallium. The combination of IC (ion chromatography) or LC (liquid chromatography) with an ICP-MS is also able to distinguish between selenates and selenites, arsenates and arsenites, which makes this method valuable for studying oxidation states of selenium and arsenic. The method favored by B&W for anions is EPA Method SW-846-9056A [10]. This method uses ion chromatography to determine anions including fluoride, bromide, chloride, nitrate, nitrite, phosphate, iodide, and sulfate. Finally, the method favored by B&W for aqueous mercury measurement is EPA Method 1631 [11], which uses cold vapor atomic fluorescence spectrometry for mercury measurement. Method 1631 is widely used by the industry, so it is easy to find a commercial lab that can perform this test. Also, mercury can be analyzed following EPA Method SW-846 6020B.

The approach described above should allow the development of a good wastewater composition profile that captures normal values and defines the range of variation. This information will greatly aid in the selection of an appropriate technology for addressing the ELG.

DISCUSSION

For the proper design of waste water treatment systems, it is important to have an indication of the range of variation as well as “normal” values for concentrations and flows. This information allows engineers to select and size the most appropriate technology for the conditions at hand, and maximizes the probability of a successful application of the treatment technology. This is particularly important for electric utilities who own power plants with wet FGD systems, as the promulgation of the EPA’s Effluent Limit Guidelines in 2015 requires that plant waste water discharge be in compliance within 2-7 years; a short time if technologies need to be selected, demonstrated, engineered, constructed, and commissioned. Initiation of a waste water characterization program aimed at developing the design data needed will greatly facilitate this process.

By nature, waste water from wet FGD systems is complex and variable. This variability makes it difficult to treat. Most power plants have a chemical-physical treatment system for wet FGD wastewater. These systems are rugged and robust, and are able to tolerate a wide variation in feed. In some cases, regulated species and allowable concentrations set forth in the new ELG may have surpassed the ability of chemical-physical treatment systems to successfully treat wet FGD waste water without the application of additional technologies [12]. Testing the waste water, as proposed, will show the performance of the existing treatment system, and will provide insight into the level of additional technology needed to meet the new requirements. Testing could lead in the direction of adding a biological treatment unit to the waste water train, or it could push the plant towards a zero liquid discharge option.

The very low allowable concentrations listed in the recent ELG have not only made waste water treatment more difficult, but they have also made testing samples more difficult. Sampling must be done with greater care, with attention to getting representative samples. Sample containers must be scrupulously clean to prevent contamination that could skew measurements. Samples must be treated to preserve them, where applicable, and need to be tested in a timely manner. Testing has become more complex and must be run by skilled chemists or chemical technicians. Though the level of effort is greater, there is still much to be gained by a wastewater characterization program. The quality of the data is important, because good decisions cannot be made from bad data.

Since the cost of chemical analysis is not trivial, the plant will ultimately have to decide how extensive to make their sample and data collection program, based on the projected benefits and what is affordable. A robust sampling program requires investment, but it pays back by “buying down risk” related to implementing new technology for addressing the ELG.

SUMMARY

In November of 2015, the EPA issued revisions to the federal Effluent Limitation Guidelines that set regulated limits for wastewater discharge from wet FGD systems in power plants. The revised guidelines set new, tighter limits on arsenic, mercury, selenium, nitrates/nitrites, and have put more rigorous demands on wet FGD Waste Water Treatment Systems, to the extent that most need to install additional technologies to meet the new limits. The window to achieve compliance with the new limits is 2-7 years, which is a short time period to select and demonstrate a new technology, then engineer, construct, and commission it in a power plant. A waste water characterization program that describes the variations in waste water concentrations and properties will facilitate the selection of appropriate technology and will increase the probability of successful application by providing a realistic design basis.

ACKNOWLEDGEMENTS

The authors would like to recognize Duke Energy, Detroit Edison, and Southern Company for many meaningful discussions, collaboration, and support over the last few years.

The authors appreciate the forums and discussions fostered by Reinhold Environmental regarding the ELG and wet FGD discharge treatment options.

The authors would like to thank EPRI, especially the leaders of the water management technology program 185, for bringing the issues regarding wet FGD effluent treatment to the forefront of the power generation industry.

REFERENCES

[1] United States Environmental Protection Agency (EPA), "Effluent Limitation Guidelines and Standards for the Steam Electric Power Genearating Point Source Category: Final Rule," in *Federal Register*, vol. 80 No. 212, Washington, D.C., U.S. Government Printing Office, November 3, 2015, pp. 67870-67871.

[2] Roush, M. J.; Glikbarg, K.; Bland, K.;, "Approaching the CCR Rule from a Water Balance Perspective," in *International Water Conference (IWC)*, Orlando, 2015.

[3] Scroggin, P.; Soller, M. J., "Solutions and Practices to Address NDPES Compliance at Coal-Fired Generation Stations in Light of EPA Proposed Effluent Limitation Guidelines," in *International Water Conference (IWC)*, Orlando, 2015.

[4] Kennedy, W. and J. Potts, "Sources of Variability in Flue Gas Desulfurization Wastewaters," in *International Water Conference (IWC)*, Orlando, 2015.

[5] Brown, Shannon R.; Johnson, Dan; DeVault, Rick, "Quantification of Colloidal Phase Metals of Concern in Limestone Forced Oxidized Wet FGD Effluent," in *International Water Conference (IWC)*, Orlando, 2015.

[6] Mon, J. L.; Hoydick, Michael T.; Wick, Stephen E., "A Root Cause Study to Determine the Source of High Gypsum Moisture," in *Power Plant Pollutant Control "Mega" Symposium*, Baltimore, 2014.

[7] Brown, S. R.; DeVault, Rick; Johnson, Dan; "ORP as a Predictor of WFGD Chemistry and Wastewater Treatment," *POWER,* vol. 157, pp. 40-42, July 2013.

[8] United States Environmental Protection Agency (EPA), "List of Approved Inorganic Test Procedures," in *Federal Register*, Vols. 72, No. 47, Washington D.C., U.S. Government Printing Office, March 12, 2007, pp. 11216 -11224.

[9] United States Environmental Protection Agency (EPA), "Method SW-846-6020B - Inductively Coupled Plasma- Mass Spectrometry," U.S. Government Printing Office, Washington, D.C., July 2014.

[10] United States Environmental Protection Agency (EPA), "Method 9056A - Determination of Inorganic Anions by Ion Chromatography," Untied States Government Printing Office, Washington D.C., February 2007.

[11] United States Environmental Protection Agency (EPA), "Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry," U.S. Government Printing Office, Washington, D.C., 2002.

[12] Higgins, T., C. Joiner, D. Fink, P. Chu, M. McCloud, L. Reid and K. Jenkins, "Flue Gas Desulfurization Physical/Chemical Wastewater Treatment for Compliance," in *International Water Conference (IWC)*, Orlando, 2015.

[13] United States Environmental Protection Agency (EPA), "FGD ICP/MS Standard Operating Procedure: Inductively Coupled Plasma/Mass Spectrometry for Trace Element Analysis in Flue Gas Desulfurization Wastewaters," U.S. Government Printing Office, Washington, D.C., 2011.

[14] United States Environmental Protection Agency (EPA), "Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels," U.S. Government Printing Office, Washington, D.C., 1996.

[15] United States Environmental Protection Agency (EPA), "Method 300.0: Determination of Inorganic Anions by Ion Chromatography," U.S. Government Printing Office, Washington, D.C., 1993.

[16] United States Environmental Protection Agency (EPA), "Standard Operation Procedure for Trace Element Analysis of Flue Gas Desulfurization Wastewaters Using ICP-MS Collision/Reaction Cell Procedure," U.S. Government Printing Office, Washington, D.C., 2013.

[17] The Babcock & Wilcox Company, Steam/Its Generation and Use, 41 ed., J. Kitto and S. Stultz, eds., Barberton, Ohio, The Babcock & Wilcox Company, 2005, pp. 35-1 to 36-13.

[18] United States Environmental Protection Agency (EPA), "Technical Development Document for the Effluent Limitation Guidelines and Standards for the Steam Electric Power Generating Point Source Category," U.S. Government Printing Office, Washington, D.C., 2015.

[19] Blyth, G.; Richardson, M.; Dene, C.; Acharya, Chethan, "Effects of Mercury Control Technologies on FGD Wastewater," in *International Water Conference (IWC)*, Orlando, 2015.

[20] Apichemical Consultants, Guide to Environmental Analytical Mehtods, Fifth ed., R. Smith, Ed., Amsterdam, New York: Genium Publishing Corporation, 2003.

[21] Gutberlet, H, "Formation of Sulfur Compounds and Sulfurnitrogen Compounds in Flue Gas Desulfurization Systems and Their Influence on the Kinetics of Sulfite Oxidation," *VGB Kraftwerkstechnik,* vol. 76, no. 2, pp. 126-133, 1996.

[22] Fogh, F.; Smitshuysen, E. F.;, "Nitrogen Speciation in FGD waste water," *VGB PowerTech,* pp. 83 - 87, July 2003.

[23] Pourbaix, M., Atlas of Electrochemical Equilibria in Aqueous Solutions, vol. 1, Pergamon Press, 1966.

KEYWORDS

Arsenic, characterization, coal-fired, detection limit, effluent limitation guidelines (ELG), mercury, methods, nitrate, nitrite, phase partitioning, power plant, selenium, total dissolved solids (TDS), trace metals, wet flue gas desulfurization (FGD), waste water treatment (WWT)