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Presented to:
Power Plant Pollutant Control "Mega" Symposium

Date:
August 19-21, 2014

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

BR-1913

Presented at the Power Plant Pollutant Control “MEGA” Symposium
August 19-21, 2014
Baltimore, MD

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ABSTRACT

While the industry is aware that variations in both boiler load and fuel have impacts on combustion processes, recent observations have shown that these changes also have significant effects upon limestone forced oxidation (LSFO) wet flue gas desulfurization (WFGD) unit operations and their associated effluents and emissions. Some WFGD units, when subjected to load swing, exhibit a much different chemistry than when run under steady conditions, particularly mercury and selenium liquid-solid phase partitioning, and the oxidative potential of the slurry. Such changes in chemistry must be considered as part of waste water management strategies. Concurrently, significant changes in WFGD chemistry associated with operational load swings can transiently result in increased mercury emissions if left unchecked. Mitigation strategies are under development to address the observed impacts that both low and swinging load operations have on WFGD chemistry, oxidation reduction potential (ORP), unit operation, mercury emissions and effluent composition.

INTRODUCTION

Recent changes in the United States power industry have lead to an increase in coal-fired power plants changing to either lower or swing load operations. Several market forces led to this change such as fuel costs, dispatched load in lieu of base load, a downturn in economic output and thus energy demand, and a desire for base-loaded alternative energy sources, such as wind power, onto the electric grid. Due to changes in flue gas flux and composition related to these changes, these variations noted above have had unanticipated impacts on both the WFGD and waste water treatment (WWT) systems. With regard to the WFGD absorber, changes in inlet sulfur dioxide (SO₂) concentration and gas flow rate impact system parameters, such as WFGD chemistry, including ORP, gypsum formation and limestone utilization. Changes in concentration of metals of concern and of the oxidizer concentration of the WFGD bleed
associated with changes in ORP result in differences in the purge stream chemistry being fed to WWT. Performance of some WWT systems may be impaired due to these conditions, such as higher selenate concentrations in the effluent from physical-chemical treatment systems or difficulties with bioreactors due to the oxidant concentration.

The majority of the WFGD systems are designed for optimal performance at steady-state, full load conditions. Therefore, the system will operate best at design conditions; departure from design may result in loss of efficiency and decreased performance, for which turndown may not be sufficient to correct in some cases. At the WFGD inlet, low and swing load operation may lead to surges in the tank level and splashing near or into the inlet, potentially leading to wet-dry interface issues at the inlet of the absorber towers. On the fluid side, reagent feed systems are sized for full load, steady-state operation. As the inlet SO₂ loading to the WFGD decreases substantially from the design basis, as may happen during conditions of low load or resulting low sulfur coal combustion, the WFGD limestone feed system could respond by entering into a mode of pulse feeding limestone slurry to the tower, potentially resulting in less efficient limestone utilization, depending on the tower chemistry at the time of such occurrences. In addition to the above concerns, the system water balance may be affected. A decrease in loading may cause a condition where the evaporative loss of the WFGD system leads to a decrease in the fresh water introduction and purging from the system. This situation has the potential to increase the total dissolved solids (TDS), and may thereby impact gypsum crystal formation and the performance of the WFGD system as a whole. The amount of oxidation air needed to provide dissolved oxygen in the absorber slurry for gypsum formation is determined by review of various design parameters, such as the operating liquid level and the dispersive capability of the agitators. As compressor turndown may be limited, the ratio of oxidation air to inlet sulfur loading (O:S stoichiometry) is often higher than needed at low load conditions, causing efficiency losses to the system in terms of parasitic power. While excess oxidation air in the system is not necessarily detrimental, if the WFGD system is already above the dissolved oxygen saturation point, this excess power consumption can result in an annual cost of upwards of hundreds of thousands of dollars.

Changes in operating load will also impact the performance of WWT systems and the final effluent composition of the treated WFGD bleed. Changes in the ORP of WFGD absorber slurry and waste water have been observed in combination with load and coal changes for some units. As the ORP changes, the speciation of many metals, including mercury and selenium, also changes. For example, the fraction of selenium that is oxidized to selenate, in lieu of selenite, increases dramatically at WFGD ORP levels above approximately 300 mV. Selenate may be difficult for some WWT systems to treat. Additionally, elevated concentrations of strong oxidizers contained in process steams with ORP levels above approximately 400 mV may negatively impact biological treatment systems.

Within the last two years, Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) has conducted two separate parametric tests on three pulverized coal-fired boilers with selective catalytic reduction (SCR), electrostatic precipitator (ESP), WFGD, and WWT systems. For the sake of this discussion, the Units are named A, B, and C. Unit A and Unit B are in the Midwest, and Unit C is located in the Southeastern United States.
PROJECT APPROACH

Field testing was initially performed at Unit A and Unit B. These units were burning several blends of Powder River Basin (PRB) and Illinois Basin (ILB) coal at varying mixes ranging from 75%/25% to 65%/35%, respectively. Unit A conducted a test burn of PRB and different high sulfur eastern bituminous coal at a 75%/25% blend as well. Online ORP measurements were taken of the WFGD absorber slurry and the process was monitored for an extended period using the site’s process data acquisition and historian system. Review of this data provided some evidence of the response of the unit to low and swinging load operation. During the course of testing, Fourier Transform Infrared Spectroscopy (FTIR) measurements were taken to provide information on the chemical speciation of the flue gas. During the course of this testing, impacts on the amount of oxidation air introduced into the tower, fly ash introduction to the WFGD absorber slurry, and some changes to upstream parameters were explored.

Field testing was performed at Unit C following the other units. Unit C burned a high sulfur ILB coal for the duration of the test. FTIR data was collected at the WFGD inlet for a portion of the test. Process data, including in situ ORP measurements of the WFGD absorber slurry, was monitored for an extended period, during which the responses of the unit to variable load operation as compared to steady-state operation were observed. Fly ash introduction to the WFGD, ESP performance and oxidation air injection rate were tested.

EXPERIMENTAL METHODS

Gas-Phase Analysis

Significant data was obtained from the process data acquisition and historian systems for all units tested.

Gas-phase FTIR monitoring was performed at the WFGD inlet during parametric testing. This technique provides real-time, continuous data about flue gas composition. For this testing, the FTIR probe was positioned in a test port near the end of the inlet duct.

Chemical Analysis of WFGD Slurry Samples

Chemical analysis was run on samples from Unit A and Unit B. A 0.45 µm filter was used to separate slurry filtrate from solids at process temperatures using a syringe filter. Samples of absorber slurry were also taken. Upon collection, samples were analyzed for pH, dissolved oxygen (DO) content, ORP and conductivity.

Anion analysis was conducted on slurry filtrate samples by EPA method 300.0, using ion chromatography (IC). Anions measured included: fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulfate.

Slurry samples were analyzed for metals composition by EPA 6020A/EPA 200.8/EPA 1638 using collision reaction cell (CRC) Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Slurry filtrate was analyzed to determine the concentration of dissolved metals. Samples of the complete slurry were digested using HF to determine the total concentration of each metal within
the slurry (filtrate and solids). Species analyzed for included: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sr, Ti, Tl, U, V, W, and Zn.

Quantification of total and dissolved mercury within the WFGD absorber slurry samples was done by a modification of EPA Method 1631e. Samples to be tested for dissolved mercury were acidified with BrCl and heated in an oven at 100 °C for one hour. Samples that remained a pale yellow color were diluted and analyzed by purge-and-trap cold vapor atomic fluorescence spectroscopy (CVAFS), whereas samples that remained clear after this treatment were spiked with additional BrCl and heated until they retained the pale yellow color. Sample preparation for total mercury measurement was accomplished by a strong acid microwave digestion including HNO₃, HCl and HF, and subsequently diluted into dilute BrCl for analysis by purge-and-trap CVAFS.

Selenium speciation was performed using an ultra high-performance liquid chromatography (UHPLC)/triple quadrupole inductively coupled plasma mass spectrometer (ICP-MS). For each sample, separation of the various oxidation states of selenium occurs on the specially designed liquid chromatography column and method, and as each selenium species elutes from the liquid chromatography column, it is quantified by the ICP-MS as Se-78.

Total oxidizer concentration was measured by a nonselective titration method.

RESULTS AND DISCUSSION

Flue Gas Flux

As the load changes in coal-fired power plants in response to demands from the grid, the amount of fuel combusted varies. Naturally, this variance causes a change in the amount of flue gas flowing through the air quality control systems (AQCS) per unit of time, the flue gas flux. This change in flux can impact the efficiency and performance of various unit operations within the AQCS, especially the WFGD units.

During field testing on Units A and B, WFGD absorber chemistry changed in response to changes in the overall process. Some of these changes correlated with changes in known parameters of upstream unit operations. Data on the system performance in response to load changes was also collected. On Unit C, some of these parameters were explored. A strong correlation between absorber slurry ORP and load change was observed on Unit C (Figure 1). ORP is a function of the ratio of the activity of total oxidizers over the activity of total reducing agents in a solution. Until recently, oxidation air was thought to be the primary source of oxidizer and that there should be a direct, almost linear relationship with ORP and oxidation air injection rate. Though the dissolved oxygen provided by oxidation air is an oxidizing agent, it is not the strong oxidizer that pushes the ORP above 400 mV.

Based on results from the recent field testing conducted at the three units discussed in this paper, the current working model is that while oxidation air may provide some control over ORP to a lower value, attempts to use this variable alone as a complete control strategy are non-ideal. If a WFGD system is operated at or near the region of full oxidation, but not above as is a normal operation, oxidation air could be used to mitigate some ORP spikes, but the likelihood of scaling,
gypsum formation problems and other operational concerns will more than likely increase significantly. Under some conditions, turndown of the oxidation air compressors may be limited such that effective control of ORP by this method alone would not be feasible.

**Figure 1. Unit C ORP Decrease with Steady-State Conditions**

**Comparison of WFGD System and Load Swings**

Mathematical modeling was done to prepare mass balances for some of the conditions observed on Units A and C at various loads and inlet SO₂ concentrations. Unit B is a sister to Unit A, therefore modeling of this unit would have been redundant. Some inputs obtained from field data include inlet SO₂, loading, and pH. Table 1 provides an overview of these inputs and corresponding results. The average value of the ORP from the field test data at each condition is also given in this table for reference.
Table 1. Comparison of Different Conditions and WFGD Parameters

<table>
<thead>
<tr>
<th>Unit</th>
<th>Inlet SO₂ (ppm)</th>
<th>Boiler Load (MW)</th>
<th>Swinging Load (yes/no)</th>
<th>SO₂ Removal (%)</th>
<th>Purge Flow (gpm)</th>
<th>pH</th>
<th>ORP (mV)</th>
<th>Ox Air to Reaction Tank</th>
<th>Residence Time (hr)</th>
<th>Reagent Flow (gpm)</th>
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<tr>
<td>Unit A</td>
<td>1276</td>
<td>825</td>
<td>no</td>
<td>97</td>
<td>248</td>
<td>5.6</td>
<td>-</td>
<td>Design</td>
<td>17.5</td>
<td>232</td>
</tr>
<tr>
<td>Unit A</td>
<td>568</td>
<td>590</td>
<td>no</td>
<td>97.7</td>
<td>75</td>
<td>5.6</td>
<td>227</td>
<td>Design</td>
<td>52.4</td>
<td>78</td>
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<tr>
<td>Unit A</td>
<td>598</td>
<td>590</td>
<td>no</td>
<td>97.5</td>
<td>75</td>
<td>5.5</td>
<td>503</td>
<td>Design</td>
<td>50.1</td>
<td>81</td>
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<tr>
<td>Unit A</td>
<td>517</td>
<td>688</td>
<td>yes</td>
<td>97.4</td>
<td>98</td>
<td>5.4</td>
<td>532</td>
<td>Design</td>
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<td>77</td>
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<td>456</td>
<td>yes</td>
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<td>5.4</td>
<td>556</td>
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<td>642</td>
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<td>5.6</td>
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<td>60</td>
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<td>yes</td>
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<td>100</td>
<td>5.9</td>
<td>560</td>
<td>Design</td>
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<td>599</td>
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<td>96.1</td>
<td>100</td>
<td>5.9</td>
<td>543</td>
<td>Design</td>
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<td>183</td>
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<tr>
<td>Unit C</td>
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<td>600</td>
<td>yes</td>
<td>98.0</td>
<td>100</td>
<td>5.9</td>
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<td>Design</td>
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<td>598</td>
<td>no</td>
<td>97.8</td>
<td>100</td>
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<td>189</td>
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<td>no</td>
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<td>125</td>
<td>5.9</td>
<td>177</td>
<td>Design</td>
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<td>206</td>
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<td>Unit C</td>
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<td>600</td>
<td>no</td>
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<td>150</td>
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<td>Design</td>
<td>20.7</td>
<td>193</td>
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<td>no</td>
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<td>5.9</td>
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<td>21.2</td>
<td>192</td>
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<tr>
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<td>150</td>
<td>5.6</td>
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<tr>
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<td>no</td>
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<td>140</td>
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<td>192</td>
<td>Design</td>
<td>21.3</td>
<td>181</td>
</tr>
</tbody>
</table>

The information provided in this table is a snapshot, assuming steady-state, and ideal conditions. A number of observations may be drawn from this data. First, a wide spread in ORP exists at the various parameters noted. Unit C exhibited a higher ORP level during days when the load had either been ramped up or ramped down. On the days when the load was held steady, in this case at full load, the ORP readings remained low. On Unit A, different ORP profiles were observed in conjunction with similar loading conditions. This shows that some of the factors controlling WFGD ORP are not occurring within the WFGD absorber reaction tank, but must be occurring upstream of the system.

On Unit C, a 4-hour test was performed wherein the oxidation air was increased to 1.4x the design amount. This had no affect on ORP, leading to speculation that the system was already over-feeding oxidation air into the reaction tank. Additionally, a short 10-minute test was also conducted in which the oxidation air was turned completely off. Although off-set by a few minutes, the pH and ORP dropped drastically. Once the pH decreased, the reagent feed flow increased as expected. Both parameters recovered in a few minutes once the oxidation air was restored to the design condition based on review of the plant’s data.

One test on Unit C was run at almost half of full load conditions (~600 MW). Immediately following this test, the load was ramped up to full load for another test. Both tests were at swinging load conditions since the unit was also at full load immediately preceding the low load test. With the lower loading, and subsequently lower sulfur loading, the % SO₂ removal increased and the reagent flow decreased in comparison to full load conditions when pH was held constant. These results were expected. ORP, unexpectedly, was unaffected and remained at high levels for both tests, leading to speculation that the swinging load was in some way responsible.
Unit A was burning a coal blend significantly lower in sulfur than design parameters accounted for, leading to decreased reagent demand and feed rate, and decreased purge rate to maintain chloride concentration. In contrast, Unit C exhibited an inlet SO₂ flux in excess of the unit design in some cases, and lower in others. Such inconsistency in unit load and SO₂ concentration leads to variance in the demand for limestone reagent and purge rate.

WFGD Absorber Reaction Tank Chemistry

The absorber slurry within the absorber reaction tank may be considered to behave in a manner similar to a continuously stirred tank reactor (CSTR). The flue gas is the source of constituents which are captured within the WFGD.

Coal contains chlorides and other halides. After combustion, these constituents become gaseous compounds that are captured by the WFGD, where they enter the fluid phase of the slurry and cycle up in concentration. As dissolved ions, the halides contribute to the absorber slurry ORP. Thermodynamic simulations demonstrate that, at typical scrubber slurry temperatures of 125 °F and a chloride concentration of ~12,000 ppm, a nominal ORP value of 200 mV is expected just from this salt concentration. Other chemical species would add or subtract from this base oxidative potential, and the low range of the LSFO WFGD slurries is often found near this level.

From the information gathered by B&W PGG over the past several years, the normal and desired operating ORP in most WFGD systems is between 150 to 300 mV. The interesting correlation from the model of the CaCl₂ salt water system, as stated above, is that the ORP predicted by this model is within the normal average of an actual operating system, with deviance from this value attributable to other known slurry constituents for the low ORP regime. One could deduce that all of the dissolved species, along with other factors, are adding and/or subtracting from the total ORP of the system, which would indicate that chemistry and blow down rates may have just as much significance as upstream factors. For example, the absorption of the SO₂ from the flue gas adds sulfite, a reducing agent. Oxidation air is added as an oxidizing reagent for the conversion of sulfite to sulfate. The calcium sulfate dihydrate, or gypsum, is removed from the system through a dewatering process.

Limestone reagent is added to the system to provide both a base for reaction with the acid resulting from SO₂ absorption, as well as calcium for the precipitation of gypsum. At very low loads and sulfur levels significantly below design, reagent feed will be slowed (Table 1).

However, none of the species commonly considered in WFGD chemistry would yield the high ORP level (>400 mV) being measured at many field sites. One or more strong oxidizers must be present in the absorber slurry, at sufficiently high concentrations, for the observed ORP to occur. The source of the strong oxidizer(s) appears to be upstream of the WFGD absorber.

**ORP and Oxidizer Concentration**

A parameter of interest when reviewing WFGD chemistry that becomes especially important for treatment of WFGD blowdown is ORP. As previously mentioned, ORP is a measure of the oxidative strength of a solution, or the electrochemical potential of the solution. One may calculate this potential using the Nernst equation (Equation 1), though this expression becomes
complicated in application to multi-component unsteady-state, non-equilibrium systems such as the WFGD slurry.

**Equation 1. Nernst Equation**

\[ E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln(Q) \]

where:
- \( E_{cell} \) = electrochemical potential of the cell
- \( E_{cell}^0 \) = standard electrode potential
- \( n \) = number of moles of electrons transferred
- \( F \) = Faraday constant
- \( Q \) = reaction quotient

ORP is proportional to the natural log of the ratio of the activities of oxidized species to reduced species. A rough approximation may be made by comparing the concentrations of the oxidized and reduced species in solution (Equation 2). Unlike some measurement techniques, ORP is not selective of any one specific chemical species. It is a measurement based upon the properties of the solution as a whole. Further, as a strongly oxidative solution is brought into contact with another solution maintained at a lower ORP, and possibly containing strong reducing agents, the two solutions will react and a portion, if not all, of the strong oxidizer in solution will be consumed. Therefore, non-selective titrations methods are often used for quantification of strong oxidizers in WFGD absorber slurry.

Strong oxidizers have been measured within the absorber slurries of operating WFGD units, including Units A and B; these measurements were not made on Unit C. Strong oxidizer concentrations on the order of 400 mg/L were measured at Unit A, when the ORP had just reached a high level.

**Equation 2.**

\[ E_{cell} \propto \ln \left( \frac{\text{oxidized material}}{\text{reduced material}} \right) \]

where:
- \( E_{cell} \) = electrochemical potential of the cell

As previously mentioned, normal, or low, ORP conditions for a LSFO WFGD is largely a function of halide and sulfite concentration, providing an ORP near 150 to 300 mV. If ORP were to fall below zero, reducing conditions would exist and one may infer that oxidation would have been lost and gypsum formation would cease. At low positive ORP values, nominally 50 mV, concern may exist that sulfite concentrations would be excessive, and scaling of tower internals could result. To ameliorate corrosion and waste water treatment (WWT) concerns, ORP should be maintained below approximately 300 mV.
The cause of high ORP, above 400 mV, is under investigation. This condition is brought about by an elevated concentration of strong oxidizers within the solution. One or more strong oxidizers is originating upstream of the WFGD, often changing in concentration as load changes. Strong oxidizers will react with other constituents of the flue gas and/or slurry, providing a mixture of oxidizers within the reaction tank and likely within the flue gas.

One observation regarding the ORP of absorber slurry is that it appears to change rapidly, and with a characteristic profile. With large volumes of slurry held within the tank, it can take many hours to days for significant changes in chemistries within the system to be observed. In contrast, absorber slurries operating at low ORP (~200 mV), have been observed to increase in electrochemical potential to a high ORP regime (>400 mV) in a very steep sigmoidal pattern over time, often reaching the high ORP profile within a matter of hours. This pattern was observed by B&W PGG during field testing at Units A and B, with Unit C repeating this pattern prior to and after the test period (Figure 1, Figure 2).

This plateau-like shape may be occurring at an equivalence point for the given tower pH and slurry constituents. The normal operating ORP condition is between 150 to 300 mV. As upstream system operational factors result in the creation of strong oxidizer and its addition to the WFGD absorber slurry, the slurry exhibits little resistance to an increase in ORP. This signifies dominance of the strong oxidizer and negligible activity of reducing species, in comparison. Such plateau-shaped curves for ORP as a function of concentration are often observed in chemistry to determine when a volume of solution has become fully oxidized.9
Due to the high relative activity of the strong oxidizers in comparison to reducing species, return of the slurry ORP to normal operating conditions after the cessation of strong oxidizer addition is slow. When the ORP decreases, going from a high to a low profile, the time needed to fully return to lower ORP conditions is often much longer, slowly lowering over a period of days. Since the ORP of operating sister units have been observed to change in response to a shared recycle, the inference may be drawn that the oxidant partitions in the dissolved phase of the absorber slurry. When concentration of oxidants is just over the equivalence point, decay to a lower ORP profile may be somewhat quicker than when the concentration of oxidants is in significant excess. Some of the strong oxidizer can be consumed by reaction with chloride. However, the kinetics of this reaction appear to be slow.

**Residence Time and Purge Rate**

The purge rate of many WFGD systems is often set for a solids concentration, as this becomes a limiting factor with high sulfur, full load conditions. Variability does exist in the secondary dewatering system, which is primarily used to control the build-up of dissolved species, such as chloride. As load decreases, the purge flow needed to maintain these concentrations likewise decreases (Table 1). Unfortunately, as load decreases, chloride concentrations may no longer be the limiting factor in determining the secondary dewatering purge rate. For example, fines may
build up, which can negatively impact gypsum crystal formation in the slurry. Increased purge rates, above those predicted to maintain chloride concentration below a certain threshold, may be needed for many WFGD systems operating at both lower loads and inlet sulfur concentrations than design.

In an attempt to explain the purging of the strong oxidizers from the WFGD system, a comparison could be made between the behavior at Site A and Site C. Site C had a high ORP condition prior to the start of the parametric testing, but within the first 24 hours, the ORP decreased at a steady rate to the lower level. This is indicative of the removal of the upstream oxidizer and analogous to watching the response of a dye trace experiment in a CSTR. One parameter this model affords for system comparison is space time, a ratio of the slurry volume within the tank to the volumetric flow rate of the purge stream (Equation 3). The space time of each unit per operating volume and the purge rates encountered at low inlet sulfur loadings is summarized in Table 2.

**Equation 3.**

\[
\tau = \frac{V}{\nu}
\]

where:
\(\tau\) = space time
\(V\) = volume
\(\nu\) = volumetric flow rate

<table>
<thead>
<tr>
<th>Unit</th>
<th>ART Volume (gal)</th>
<th>Average Volumetric Purge Flow Rate (gal/hr)</th>
<th>Space Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Units A &amp; B</td>
<td>5.5 x 10^5</td>
<td>6.0 x 10^5</td>
<td>122</td>
</tr>
<tr>
<td>Unit C</td>
<td>8.5 x 10^5</td>
<td>4.5 x 10^3</td>
<td>142</td>
</tr>
</tbody>
</table>

By comparing the results of these calculations, one observes that the low loading and low sulfur conditions encountered during variable operation causes extended residence time of many dissolved species, including oxidant, within the absorber reaction tank. Units A and B had higher purge rates and lower space times than Unit C. Therefore, the WFGD slurry in the reaction tank of Unit C would be expected to build and maintain concentrations of inerts and of the oxidizer in the system due to the lower purge rates.

The CSTR model is a good approximation for determining the shape of the curve for purging oxidant from the system (Figure 3). For a CSTR, the simplifying assumption of complete mixing is made, thus the concentration in the tank is assumed to be equal to the concentration at
the discharge and in process samples. Using values for the initial concentration and for space
time, the concentration of an inert species within the reaction tank at any given time may be
calculated by Equation 4.

\textbf{Equation 4.}^{11} 

\[ C(t) = C_0 e^{-t/\tau} \]

where:
\( C(t) = \text{Concentration of an inert as a function of time} \)
\( C_0 = \text{initial concentration} \)
\( t = \text{time} \)
\( \tau = \text{space time} \)

\textbf{Figure 3. Predicted Concentration of an Inert Species in the Unit A and C WFGD Slurry
after Input of the Inert Species to the System has Stopped}

In practice, however, the curve is often slightly steeper. Such deviations can be attributed to
system idealities and the fact that ORP is based on the natural log of relative concentrations of
species that change rapidly at the equivalence point.

\textbf{Oxidation Air}
The amount of oxygen that dissolves into solution from the injected oxidation air depends on a
number of factors, including, but not limited to, the solubility of oxygen, the dispersive
capability of the agitators, bubble size and air bubble residence time. Excess oxidation air is
added to the system to ensure that complete oxidation occurs, leading to wallboard grade gypsum
and minimizing the risk of sulfite scaling and limestone blinding. If insufficient oxidation air is available, levels of sulfite would increase within the absorber reaction tank.

At lower sulfur loading, the actual O:S stoichiometry may be significantly above that required for gypsum formation since the oxidation air is often added to the absorber reaction tank at a fixed rate, regardless of the boiler load or sulfur loading to the absorber. This phenomenon was evident from review of data collected during the field tests at Units A, B and C. Table 3 presents the actual and required O:S stoichiometric ratio of these units at various operating conditions. In some cases the oxidation air was substantially higher than required.

### Table 3. O:S Stoichiometry for Various Load Conditions

<table>
<thead>
<tr>
<th>Unit</th>
<th>Condition</th>
<th>Oxidation Air Flow (scfm)</th>
<th>Actual O:S</th>
<th>Min. Predicted Required O:S</th>
<th>pH</th>
<th>ORP (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Full Load</td>
<td>15,493</td>
<td>3.64</td>
<td>3.29</td>
<td>5.6</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>High Load</td>
<td>15,732</td>
<td>16.7</td>
<td>3.4</td>
<td>5.6</td>
<td>227</td>
</tr>
<tr>
<td>A</td>
<td>Full Load</td>
<td>15,732</td>
<td>15.4</td>
<td>3.4</td>
<td>5.4</td>
<td>532</td>
</tr>
<tr>
<td>A</td>
<td>Low Load</td>
<td>15,732</td>
<td>77.6</td>
<td>3.4</td>
<td>5.4</td>
<td>556</td>
</tr>
<tr>
<td>A</td>
<td>Medium Load</td>
<td>15,732</td>
<td>22.7</td>
<td>3.4</td>
<td>5.6</td>
<td>486</td>
</tr>
<tr>
<td>C</td>
<td>Low Load</td>
<td>14,800</td>
<td>6.0</td>
<td>2.4</td>
<td>5.89</td>
<td>560</td>
</tr>
<tr>
<td>C</td>
<td>Full Load</td>
<td>14,800</td>
<td>3.3</td>
<td>2.4</td>
<td>5.89</td>
<td>543</td>
</tr>
<tr>
<td>C</td>
<td>No ox air</td>
<td>0</td>
<td>0</td>
<td>2.4</td>
<td>5.55</td>
<td>87</td>
</tr>
</tbody>
</table>

If the O:S stoichiometric ratio became low enough due to limited oxidation air or an increase in sulfur flux through the system, sulfites could build, thereby lowering ORP. As ORP corresponded to changes in flue gas flux at Unit C, calculation of the actual to required flue gas flux was necessary. Analysis of these results indicates that sufficient oxidation air was available at all loadings for Unit C, except the period during which the compressor was taken offline and the ORP decreased to 87 mV (Table 3). Therefore, another factor is responsible for the oxidizer content of the absorber slurry.

The potential impact of excess oxidation air injection on ORP, especially at very high values for O:S stoichiometric ratio, was explored. The amount of oxygen that will dissolve into the reaction tank is limited. Once saturation has been reached, excess oxidation air will bubble out...
of the top of the reaction tank, not resulting in a change in ORP level. At Unit A, parametric testing of the dissolved oxygen concentration as a function of oxidation air compressor setting was conducted. Results are presented in Table 4. Based on these results, the authors infer that additional oxidation air did not appreciably change ORP at Unit A, indicating that the unit was already at near saturation conditions for dissolved oxygen. Further, oxidation air turndown at this Unit was insufficient to afford any measure of ORP control with the current equipment configuration.

Table 4. Results of Oxidation Air Testing at Unit A

<table>
<thead>
<tr>
<th>Oxidation Air Blower Setting</th>
<th>Dissolved Oxygen Concentration (mg/L)</th>
<th>ORP (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>5.67 ±1.07</td>
<td>550</td>
</tr>
<tr>
<td>Diffuser at 45% of Maximum</td>
<td>5.15 ±0.49</td>
<td>530</td>
</tr>
<tr>
<td>Diffuser at 72.5% of Maximum</td>
<td>5.07 ±0.19</td>
<td>510</td>
</tr>
<tr>
<td>Diffuser at 90% of Maximum</td>
<td>5.09 ±0.34</td>
<td>530</td>
</tr>
</tbody>
</table>

Gypsum Chemistry
Another important factor for consideration at low and swing load operation is gypsum crystal formation within the WFGD absorber reaction tank. To control the rate of gypsum crystal growth within an absorber, maintenance of system chemistry is crucial. Gypsum crystal formation in a WFGD results from nucleation due to several conditions. The gypsum relative saturation and concentration of fines within the system play important roles in crystallization. During periods of low load operation, the rate of chloride level build-up is lower than at full load conditions because less coal is being combusted, decreasing chloride addition to the system. The design basis for chloride purge rate includes the blow down for the fines, which consists of inerts from the limestone and ash particles. At steady state/full load, the chloride levels increase faster than the fines, which allows operations to take care of both chloride and fines with anticipated purge rates. However, lower sulfur fuels and lower sulfur loading to the WFGD may allow for fines to proliferate faster than the chloride levels. With most operations primarily concerned with blow down for chlorides, the recycle of the primary hydroclone overflow back into the WFGD system is possible at lower chloride levels. Types of nucleation include homogenous and heterogeneous.

Homogenous growth is favorable with the critical size of the crystals being dependent on the supersaturation of the slurry. This type of nucleation, where gypsum crystals grow from other crystals, may be supported through recycle of gypsum crystals back to the absorber, seeding the fluid for growth. The calcium to sulfate ratio should be kept fairly uniform, and in a region of supersaturation that promotes gypsum crystallization but which does not lead to excessive
scaling. During the design phase of the WFGD systems, mechanical attrition is a set parameter due to the size of the pumps and agitators relative to the volume of the absorber.

Gypsum crystal growth on fly ash may be thermodynamically more favorable when compared to growth on other gypsum crystals.\textsuperscript{13} With the intrusion of fine particles, such as inerts, the crystal growth may deviate from homogenous to heterogeneous, that is, precipitation of the crystals onto non-like particles, e.g., ash, limestone inerts, or other foreign particles.\textsuperscript{13} The ash loading in the system should be limited to maintain crystal morphology. An excess of fine gypsum crystals will lead to a smaller overall particle size distribution, as many small crystals grow slightly as compared to appreciable growth from that mass of gypsum crystallizing onto fewer nuclei. Therefore, WFGD purge rates and upstream particulate collection efficiency play important roles in gypsum crystallization.

**Wet-Dry Interface**
The variation in boiler load may lead to differences in flue gas flow through the WFGD towers. These changes in flue gas flux may cause significant slurry surging and waves in the absorber reaction tank that result in splashing into the inlet of the towers if the operating liquid level is near enough to the floor of the inlet. On the corners of the inlet, low flow conditions or rapid changes in the boiler ramp rates could have the potential for formation of eddies around the side deflectors. These eddies lead to low pressure zones which create areas of liquid layout and deposit formation. The liquid layout in the inlet area may lead to scale formation due to the evaporation of water and an increase in the relative saturation of the gypsum crystals.

**Flue Gas Chemistry and Upstream Factors**

**Impact on ESP Performance and Subsequent Impact on WFGD Chemistry**
Optimal ESP operation depends on steady-state conditions. Deviation from these conditions may lead to changes in the ESP performance. Coal variations may result in subtle changes in fly ash chemistry and collection efficiency. Fuel and load variation have caused many ESPs to be operated outside of design parameters. Variation from the design parameters of the ESP may lead to unintended downstream conditions, with the elevated ORP levels in the WFGD and WWT systems being the primary concern.

**Fly Ash Concentration**
The addition of excess fly ash to the absorber slurry has been hypothesized as a possible cause of high ORP. Fly ash contains relatively high concentrations of transition metals. Presence of these transition metals in solution could provide for the initiation step required for the free radical formation cited as one cause of strong oxidizer formation.\textsuperscript{12} Therefore, this parameter was examined at Unit C. As part of parametric testing at this unit, under full load, steady-state operation, ESP efficiency and boiler O\textsubscript{2} set point were altered independently, resulting in a significant increase in opacity. With this increase in opacity, significant pulses of fly ash were fed to the scrubber, with a slight step feed of increased fly ash loading to the WFGD for a period of hours thereafter. As can be observed in Figure 4, these increases in fly ash loading did not result in a significant change in the observed scrubber slurry ORP. Therefore, analysis of these results leads to the conclusion that increased fly ash loading is not a leading factor in WFGD slurry ORP.
Observations made on Unit A, under less controlled conditions, corroborate the finding that increased fly ash concentration within the absorber slurry is not a leading cause of high ORP. Intermittent increases in opacity due to maintenance issues with the particulate collection device have been observed. These increases in opacity would lead to additional fly ash within the WFGD absorber slurry. During such occurrences, absorber slurry ORP does not substantially change.

**ESP Factor**
Some factors of ESP operation tested at Units A and B appear to result in changes in WFGD chemistry. Certain changes in ESP operation coincide with an increase in the WFGD slurry ORP from a low to a high profile, with the ORP decreasing back to normal levels when the system is returned to normal conditions. This response seems to be repeatable, having been observed on multiple occasions on each unit.

The ESP performance changes based upon coal composition and gas flux. During low and swing load operation, the ESP may make changes to flue gas chemistry that differs from normal operation. The chemistry of the fly ash also seems to be a factor adding into ESP performance. B&W PGG correlated ESP operating data into an ESP Performance Factor to understand how
known changes in ESP operation may be captured in process data, and their relationship to scrubber chemistry. This provides a general metric, attempting to express changes in the ESP performance that may result in changes in scrubber slurry ORP in a widely applicable manner. This ESP Performance Factor is provided, along with the boiler load and WFGD slurry ORP for Units A and B in Figure 5 and Figure 6, respectively. Figure 6 also provides information about the total oxidizer concentration in the absorber slurry.

**Figure 5. Unit A ESP Performance Factor, Boiler Load, Strong Oxidizer Concentration and ORP**
The data correlations from Units A and B show an effect from both the coal blends and the boiler load. During the testing on Unit A, Unit B coal blending was uniform with a lower sulfur blend and variation in boiler load. ORP levels on Unit B remained stable and low, around 220 mV, while Unit A ORP levels rose as demonstrated in Figure 5. Around February 18, 2013, Unit B also experienced an ORP spike, which is shown in Figure 6. The ORP did return quickly to the baseline value before another spike.

An increase in the intensity of the ESP factor is observed prior to ORP increases in both units. Comparison between the ESP Performance Factor on Units A and B show both a magnitude and duration difference, with Unit A having an increase in both. This data is of interest, as it may determine how changes in ESP operation, which are often related to coal and load, can impact downstream operations. Unfortunately, being derived from field data rather than from controlled bench or pilot testing, this correlation is imperfect. It is postulated that factors of ESP performance expressed within the ESP Performance Factor have the potential to lead to an increase in oxidizer concentration in WFGD systems, and further research is planned.

Unit A became saturated with a high concentration of oxidizer present, causing the ORP levels to remain high for extended durations, in spite of a reduction of the ESP Performance Factor.
B ORP increased briefly, but the higher load and subsequent blow down rate from the WFGD system brought in more fresh water to dilute the system and thus, reduce the ORP levels. The continued elevation of the ESP Performance Factor however, may have lead to the second spike in the ORP of the WFGD system and the longer duration of higher ORP due to a potentially higher concentration of oxidizer.

Parametric testing on Unit C differed from prior studies in that both the load and coal blend were held constant for the week of testing. The Unit C testing was part of a planned 30-day coal test. The parametric testing occurred during the third week of the test burn. Load for the first two weeks varied hourly based upon dispatched demand, and the ORP levels remained above 500 mV for most of the two-week period. Upon start of the parametric testing, ORP levels had nominally been at 500 mV. The steady-state, full load boiler conditions allowed the ORP levels to decrease at a uniform rate which is indicative of the upset condition removal. One may summarize that by holding both boiler load and coal blend steady, the oxidizer concentration in the WFGD decreased on Unit C.

**Nitrogen Speciation**

The speciation of nitrogen in the WFGD inlet may play a role in the prediction of ORP in some cases. Though often neglected in WFGD modeling, some species of nitrogen are water soluble and, depending upon which species and the concentration thereof, could be a source of additional oxidants or reductants introduced to the scrubber. Upon contact with water, NO₂ may hydrolyze to form HNO₂ and HNO₃, both of which are water soluble. NO has a low but non-negligible solubility in water, and the ratio of NO to NO₂ in flue gas has been previously explored in simulated WFGD conditions and found to have some possible impact upon system oxidation.¹⁶ Some N₂O, if present, may also dissolve in water. FTIR analysis was run during field testing to determine how significant of a contributor the nitrogen speciation was to WFGD chemistry.

Figure 7 provides the nitrogen speciation at the WFGD inlet of Unit C for a portion of the testing. The unit was at steady state during these conditions. The nitrogen speciation did not appear to significantly change in a manner that correlated with ORP at this unit.
Impacts upon Waste Water Treatment, Mercury and Selenium

The WFGD absorber slurry purge stream goes through process operations, such as hydroclones, to separate out gypsum solids. A portion of the remaining fluid, depending upon halide concentration or other process limitations, is sent to waste water treatment for processing.

The ORP of the WFGD absorber slurry will determine the phase partitioning and speciation of many metals of concern for WWT, including mercury and selenium. Therefore, implementation of control of the WFGD chemistry – including ORP – could improve waste water treatment operations.

**Mercury**

Field test data indicates that, in the absence of additives, mercury preferentially partitions with the absorber slurry solids at low ORP conditions. With an increase in ORP, mercury is found more readily with the absorber slurry filtrate, presumed to be in the dissolved or colloidal phase because it passes through a 0.45 µm filter. Therefore, maintaining lower ORP values will cause lower loading of mercury to WWT systems, lowering the risk of an operating unit exceeding desired mercury limits in their effluent discharge.
Further, mercury is a very electrochemically active species. Brief evolution of mercury into the
gaseous phase has been correlated with transient ORP conditions. As WFGD ORP increases or
decreases, mercury may be released. Sequestration of mercury to a stable form within the slurry
solids is preferable to prevent such releases, and additives are available on the commercial
market for this purpose.

**Selenium**

At ORP values below ~300 mV, selenite is generally observed to be the dominant form of
selenium within WFGD absorber slurry and blowdown. This form is generally treatable by
physical-chemical precipitation methods. However, as the system ORP increases, the selenate
form of selenium is favored at scrubber conditions.6

**Oxidizer Concentration**

At elevated ORP conditions, the absorber purge stream will contain a high level of unreacted
oxidizers. These oxidizers will continue to react with purge stream constituents. As the
oxidizers react with halides in solution, halogen-containing gas is released and pH drops. This
decrease in pH may result in an increased amount of base addition required during WWT
pretreatment, which would increase treatment costs for the plant. Further, the oxidizers may
impair bioreactor performance for a time in some cases.

**Mitigation Strategies**

To facilitate more cost effective and responsive waste water treatment operation, controlled
bleed stream chemistry from the WFGD is desired. This chemistry should be maintained at a
low ORP (<300 mV) regime to keep the mercury and selenium in their preferred insoluble form.
This need is complicated by the changes in coal chemistry, low load and swinging load operation
which are all regular conditions at many power plants today.

One method that could be used to respond to these changes is system optimization. By utilizing
feed forward signals regarding process changes upstream of the WFGD, various measures can be
taken throughout the system to dampen and to control the overall response to transient conditions
that would normally result in increased ORP.

**SUMMARY**

The cause of high ORP in WFGD absorber slurry is under active investigation. As is evident in
the data and theories presented in this paper, ORP spikes experienced by numerous stations have
proved difficult to predict with any certainty. The field tests conducted by B&W PGG and
review of process data acquisition and historian system data from an abundance of other multiple
plants have lead to a theory of load swinging and fuel blending as a potential driver for the ORP
events. The three units discussed in this paper showed ORP spikes, with Unit C showing a
steady decrease after an ORP spike, signifying the removal of the stimulus. The effects of load
swing on the flue gas speciation and the responses from the equipment, such as the ESP, may
possibly be leading to the ORP spikes. ORP is a function of the natural log of the ratio of the
activities of oxidizers and reducers in solution. At lower ORP levels, the slurry ORP is
dominated by the concentrations of calcium ions, chloride ions, sulfite ions, and dissolved
oxygen. As strong oxidizer is added to reach appreciable levels, the system ORP increases. In
an ORP range between 300 and 500 mV, the system seems to reach an equivalence point, and ORP dramatically increases, in a sigmoidal fashion. Once the ORP is above approximately 500 mV, concentrations of oxidizers may significantly increase with little change in measured ORP. Therefore, at low WFGD ORP levels, the duration and magnitude of a stimulus required to raise the ORP is lower than at a corresponding unit at a higher ORP level. This, coupled with the decreased purge rates from lower sulfur loading (i.e., fuel blending and use of lower sulfur PRB coal), causes the WFGD chemistry not to purge correctly and results in a build-up of TDS and, potentially, oxidizer concentrations.

The issue of ORP has become prevalent in recent years due to the impact on the manganese-accelerated corrosion on the WFGD alloys. Impacts on the effluent discharge coupled with new regulatory proposals have made this an emerging issue of concern in the industry. Though some WFGD systems may have been running at high ORP levels in the past, regular in situ measurement of this parameter became more frequent due to the accelerated corrosion to which it was correlated. As data from this measurement became available, plants regularly see absorbers change ORP profiles, and some of these changes can be related to the trend towards swing load operations. There are several theorized reasons for the recent trend that include the increased capacity of the WFGD systems for SO$_2$ removal and the associated increased liquid to gas ratios, plants opting for more cost-effective energy production, variation in the coal blends, and the operation of plants with more aggressive ramp rates, rather than steady-state and full load operation.

The market conditions for a coal plant in the United States have changed with emerging environmental regulations as well as competition in a potentially unregulated power grid. Power companies are forced to look at fuel flexibility to keep generation costs as low as possible. The advent of renewable energy sources has lead to an increase in rapid changes in the plant load, which has been shown to have an impact on station operations. Due to the unpredictable nature of the renewable energy grid, plants have to become increasingly aggressive with ramp rates to keep the power stable. With nuclear plants unable to rapidly adjust load to the grid, the bulk of the grid stabilization will come from coal-fired plants.

ACKNOWLEDGEMENTS

The authors would like to acknowledge and thank Duke Energy for facilitating and hosting a portion of the field testing reported herein.

The authors would like to recognize Southern Research Institute (SRI) for running a significant amount of the chemical analyses reported herein.

The authors would like to recognize Prism Analytical for running a portion of the FTIR measurements discussed herein.
REFERENCES


KEYWORDS
Wet flue gas desulfurization, WFGD, waste water treatment, WWT, swinging load, oxidation reduction potential, ORP, oxidizer, mercury, selenium, trace metals, effluent composition, phase partitioning, gas flux

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