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Environmental

Techniques for Determining Limestone Composition and Reactivity

Limestone composition and reactivity are critical factors that determine the performance of limestone-based wet flue gas desulfurization systems. Limestone quality affects sulfur dioxide (SO_2) removal, reaction tank sizing, limestone consumption rate, and composition of the gypsum product and waste streams. Reactivity is a direct measure of how readily a limestone will provide alkalinity to neutralize the acid resulting from SO_2 dissolution in water. In this article we review your limestone analytic measurement options and discuss their relative accuracy and limitations.

Limestone is a commonly occurring sedimentary rock, predominantly composed of calcium and magnesium carbonate ($MgCO_3$) with various amounts of silicates, metal oxides, and other impurities. Mineralogically, limestone may be regarded as calcite, magnesian calcite, dolomite, or an aggregate with varying proportions of each of these minerals.

Pure calcite exists as crystals of calcium carbonate ($CaCO_3$) with a rhombohedral unit cell. A limestone becomes dolomitized as magnesium ions are integrated within the calcite matrix, magnesium substituting for calcium on a one-to-one atomic basis. Limited integration of magnesium produces magnesian calcite. Complete dolomitization occurs when an equimolar ratio of $CaCO_3$ and $MgCO_3$ exists within the lattice.

Substitution of $MgCO_3$ into the crystal matrix is an exothermic reaction. As a result, the dolomite and, to a lesser extent, magnesian calcite, are more thermodynamically stable structures than pure calcite. Therefore, the lattice strength is increased as magnesium is incorporated. Like calcite, the basic crystal structure of dolomite is rhombohedral, with magnesium occupying every other position from calcium on the cation plane.

The convention within industry has been to assume that all of the $MgCO_3$ in limestone is dolomitic, with an equimolar molar ratio of $MgCO_3$ and $CaCO_3$. Actually, the molar ratio of these species can vary considerably from crystal to crystal, and the reactivity of each crystal varies in relation to the fraction of $MgCO_3$ in the crystal. Most limestones selected for wet flue gas desulfurization (WFGD) application are highly calcitic, containing less than 5% $MgCO_3$.

Limestone for Sulfur Removal

Accurate determination of limestone composition and reactivity are crucial in the selection of reagents for WFGD applications, especially for systems producing commercial grade gypsum products. (See Seminole Generating Station story, p. 52.) Although systems can be constructed to utilize a wide range of limestone composition and reactivity, limestone quality must be

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limestone consumption rate, and WFGD system performance.

==Mineral species of interest are calcite, magnesian calcite, and dolomite. The magnesian calcite or substituted calcites range from 6% to 13% magnesium replacement of calcium in the crystal structure.== Also of concern are the silicates and metal oxides, which are inert in the WFGD process but affect gypsum purity; concentrations of these inerts in the gypsum are often limited to specific levels for commercial grade gypsum product.

Though the use of lower-quality limestone may provide an advantage in system operating cost, the benefit of these savings should be weighed against impacts on system performance. Limestone of acceptable quality is necessary for achieving design-level performance.

WFGD System Chemistry

Pulverized limestone is used in WFGD absorbers to provide alkalinity for reaction with SO_2 from the flue gas. Within a WFGD system, SO_2 dissolves into the aqueous slurry, where dissociation occurs and produces sulfurous acid. Acid undergoes a heterogeneous reaction with the surface of limestone particles, yielding calcium cations and hydrogen carbonate anions within the slurry. The hydrogen carbonate then undergoes acid-base neutralization, producing carbon dioxide (CO_2) and water. Within the absorber reaction tank — in addition to limestone dissolution, acid neutralization, and CO_2 stripping — sulfite is oxidized to sulfate, and the calcium ions, sulfate, and water subsequently react to form a gypsum product.

Gypsum composition and purity are dependent upon limestone composition. When limestone possessing low available $CaCO_3$ is fed to the system, limestone feed rates must increase to provide the same level of SO_2 removal. In so doing, both limestone consumption and the level of impurities, including $CaCO_3$, within the slurry will increase. Consequently, the gypsum purity and quality will decrease. Several means of determining limestone composition are available.

Thermogravimetric Analysis (TGA). TGA is an analytical technique that can be used to determine the proportion of different mineralogical species within a limestone sample. This method harnesses the differences in thermal decomposition temperatures of limestone constituents to determine composition by measuring weight loss as a function of temperature. As a limestone sample is heated in a stream of CO_2 gas, its weight decreases as decomposition occurs from the increased temperature. Sample weight loss is interpreted as a weight fraction of CO_2 evolved, by taking the ratio of sample weight to the total original sample weight.

Mineralogical structure affects the decomposition temperature of a compound. Carbon dioxide is evolved from $CaCO_3$ and from the $MgCO_3$ bound within dolomite and magnesian calcite at different temperature ranges (Table 1). Initially, water, organics, and impurities are driven off at low temperatures. After this point, decomposition of the carbonate species within limestone begins.

Species	Impurities	Non-dolomitic MgCO₃	Dolomitic MgCO₃	CaCO₃
Approximate decomposition temp. range	<500C	500C–650C	650C–875C	>875C

**Table 1. Approximate decomposition temperatures for limestone.** Source: B&W

It's important to note that magnesium may be bound within the dolomite or as magnesian calcite. However, precise quantification of the magnesium content within the magnesian calcite phase by TGA is difficult due to the spectrum of magnesium concentrations

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of the TGA. A strong decrease in weight is often associated with CO_2 loss from the $MgCO_3$ within the dolomitic structure. After CO_2 loss attributed to $MgCO_3$ species, CO_2 is evolved as from decomposition of $CaCO_3$, irrespective of mineral phase.

Analysis of TGA data is based upon sample weight loss as a function of temperature and the derivative of this function (Figures 1 and 2). The total sample weight loss is calculated on a CO_2 basis, providing a direct measurement of total carbonate within the sample.
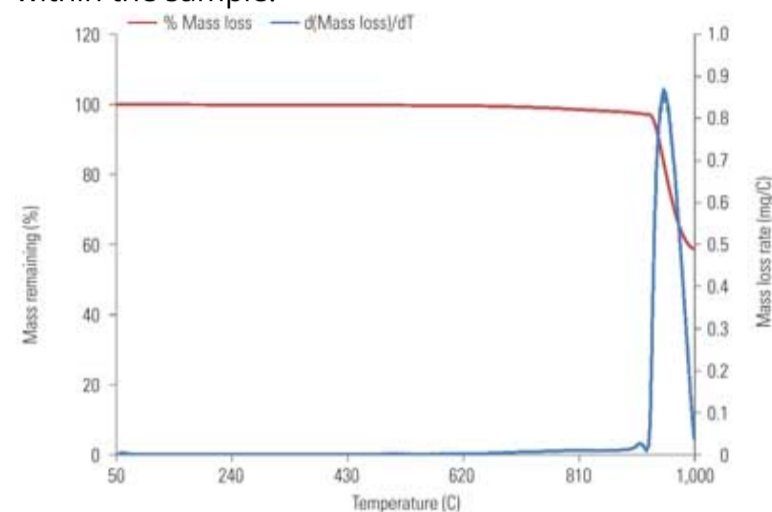
1.   **TGA data for NIST SRM 1d.** Source: B&W
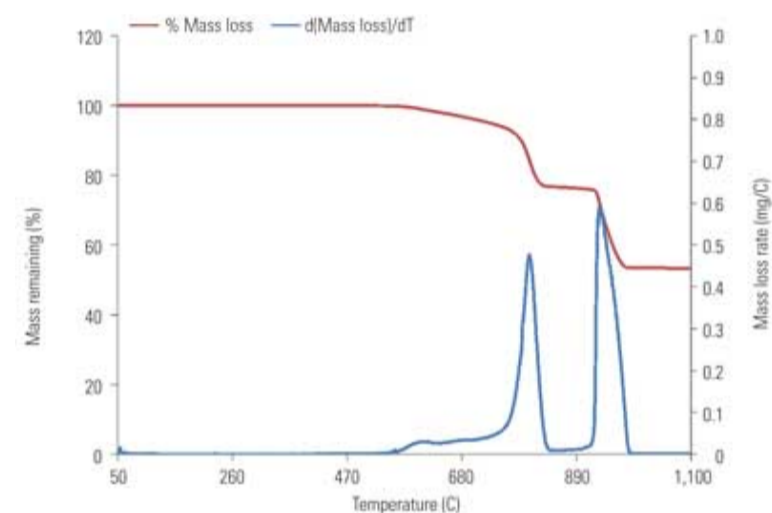
2.   **TGA data for NIST SRM 88b.** Source: B&W

The derivative of the weight loss vs. temperature function provides a means to quantify the CO_2 associated with magnesium species. The dolomitic peak is integrated to afford a value for the CO_2 weight loss assigned to dolomitic $MgCO_3$. Due to its low concentrations in limestone, the $MgCO_3$ associated with magnesian calcite seems to be outside of the TGA detection limit and indistinguishable from the baseline of this derivative function for most limestones. The difference between the total CO_2 weight loss and dolomitic $MgCO_3$ weight loss is attributed to $CaCO_3$ decomposition. Such an approximation entails grouping the $MgCO_3$ associated with magnesian calcite into the value for total $CaCO_3$.

X-Ray Fluorescence (XRF). XRF is a widely available, rapid, and cost-effective technique for elemental analysis. It also offers the benefit of quantifying many elements simultaneously, including such species as silicon and various metals.

During XRF, a specimen is irradiated by a high-energy X-ray beam. Energy is released in wavelengths characteristic of specific elements. The total energy released in each characteristic wavelength is proportional to the amount of that element present. These wavelengths are used to identify the elements present in a specimen. Concentrations of the elements are determined by relating the measured radiation to analytical curves from reference materials of known composition.

Wet Chemical Test Methods. Wet chemical test methods are used in combination to provide results that could be obtained from a single XRF or TGA analysis. These methods are often labor-

The TAPPI train is a gravimetric methodology for determining the total CO_2 fraction of a limestone sample. Oxalate titration is a method for determining the calcium content of a limestone sample. Ammonium phosphate gravimetric methodology is used to determine the magnesium content of a limestone sample.

Laboratory Testing Results

To compare the accuracy of different techniques for limestone analysis, a dolomitic limestone control (NIST SRM 88b) and an argillaceous limestone control (NIST SRM 1d) were selected for testing by TGA, XRF, and wet chemical test methods. NIST SRM 88b has a relatively high $MgCO_3$ content and exhibits low reactivity due to the dolomitic content. In contrast, NIST SRM 1d is highly calcitic and would be more representative of a WFGD reagent limestone. Multiple analytical runs were conducted on each of these limestone samples using the various techniques.

Blended samples of NIST SRM 1d spiked with NIST SRM 88b were created for TGA and XRF analysis, such that low quantities of the dolomitic stone were mixed into the argillaceous limestone, creating artificial samples with a range of dolomitic magnesium carbonate content. $MgCO_3$ content of these blends ranged from 1% to 4% by weight. These low percentages of $MgCO_3$ are representative of those found in limestones used in field units.

Use caution when comparing results from different techniques because the techniques use different physical properties of the limestone and associated assumptions, yielding different bases for quantification of individual species, some of which may be perceived as a natural bias when reviewing results.

Elemental techniques, including XRF and wet chemical methods, provide values for the total fraction of an elemental species. However, information about mineral structure is not obtained. When interpreting XRF or wet chemical results, assumptions are made by the WFGD system supplier as to magnesium carbonate partitioning within the limestone.

TGA is a destructive technique, in which differences in thermal decomposition temperature of $CaCO_3$, dolomitic $MgCO_3$ and $MgCO_3$ not bound within the dolomitic matrix are used during data interpretation to discern both mineral and chemical composition. Although it quantifies the fraction of crystal structures in the bulk sample, TGA cannot yield information as to the exact elemental composition.

Determine Total Calcium Carbonate. Quantification of total $CaCO_3$ is necessary because this is the main limestone constituent that will react in a WFGD system. Inaccuracies in this measurement translate into errors in calculating total available $CaCO_3$, which will affect the system design and performance. To compare the accuracy of each technique, testing was performed on two NIST-certified standard limestones and on six blends of these limestones (Table 2).

Limestone sample		Total CaCO₃, weight (%)			
		Values calculated based on NIST certified values	Mean value of TGA results	Mean value of XRF results	Mean value of OTM results
NIST Standard	Dolomitic limestone (NIST SRM 88b)	53.45	66.44	53.71	54.74
	Argillaceous limestone (NIST SRM 1d)	94.33	93.59	94.46	93.36
Synthetic blend	99% NIST SRM 1d, 1% SRM 88b	93.92	94.33	94.06	-
	98% NIST SRM 1d, 2% SRM 88b	93.51	93.58	93.49	-
	97% NIST SRM 1d, 3% SRM 88b	93.10	92.85	93.35	-
	96% NIST SRM 1d, 4% SRM 88b	92.69	92.60	92.46	-
	95% NIST SRM 1d, 5% SRM 88b	92.28	92.18	92.37	-
	92% NIST SRM 1d, 8% SRM 88b	91.06	90.98	90.61	-

Notes: NIST = National Institute of Standards and Technology, OTM = oxalate titration method, TGA = thermogravimetric analysis, XRF = X-ray fluorescence

Table 2.   Testing measurement accuracy. Mean CaCO3 testing

on six blends of those limestones. Source: B&W

The results showed that all methods provided an accurate estimate for the total $CaCO_3$ content of NIST SRM 1d. For 88b, XRF afforded the most accurate measurement of total $CaCO_3$, as compared to certified values. Results using the oxalate titration method were slightly higher than expected, but they were allowable. TGA results were biased high for this sample. Some of this overestimate was likely caused by the assignment of magnesium in the magnesian calcite phase to total CaO. Highly dolomitic stones are unlikely to be used in WFGD systems. Therefore, though TGA may have a bias in this range, it is an appropriate method for limestones with magnesium content in the range encountered in commercial WFGD application.

Determine Magnesium Carbonate Content. Determining magnesium content is another important aspect of limestone compositional analysis. This testing approach illustrates the fundamental differences between TGA and elemental techniques, including XRF and wet chemistry. XRF and other elemental techniques provide a value for magnesium based upon the total magnesium content detected within the species, expressed as MgO or $MgCO_3$. Industry convention is to assume that all $MgCO_3$ reported from elemental analysis is bound as dolomite in a 1:1 atomic ratio with $CaCO_3$.

In contrast, TGA is a physical technique that yields different results depending upon the degree of dolomitization of the limestone sample, as CO_2 will be evolved from highly calcitic and highly dolomitic mineralogical phases at different temperatures. Therefore, results for the dolomitic magnesium carbonate content reported by TGA should be lower than XRF results for total magnesium, expressed as $MgCO_3$. This lower value results from the difference between the total $MgCO_3$ and the $MgCO_3$ strongly bound in a dolomitic matrix, likely equating to the magnesium bound as magnesian calcite.

All three methods underestimated the total $MgCO_3$ content of the NIST 1d. This may be due to the very low concentration of $MgCO_3$ present in this sample. The six control blends were created to address this concern, exhibiting a range of $MgCO_3$ content. XRF and the ammonium phosphate gravimetric method afforded similar results for the dolomitic limestone, agreeing well with certified values. TGA results were lower for the dolomitic limestone, as this method quantifies dolomitic $MgCO_3$ rather than total $MgCO_3$ content.

We observed that average XRF results provide a better indication of total $MgCO_3$ when compared to TGA results, though some of this may be attributed to differences in mineral phase (Table 3).

Limestone sample		Total $MgCO_3$, weight (%)			
		Values calculated based on NIST certified (total)	Mean value of TGA results (dolomitic)	Mean value of XRF results (total)	Mean value of OTM results (total)
NIST Standard	Dolomitic limestone (NIST SRM 88b)	43.99	36.74	44.01	43.92
	Argillaceous limestone (NIST SRM 1d)	0.63	0.37	0.59	0.42
Synthetic blend	99% NIST SRM 1d, 1% SRM 88b	1.06	0.70	1.08	-
	98% NIST SRM 1d, 2% SRM 88b	1.50	1.07	1.40	-
	97% NIST SRM 1d, 3% SRM 88b	1.93	1.50	1.99	-
	96% NIST SRM 1d, 4% SRM 88b	2.36	1.90	2.43	-
	95% NIST SRM 1d, 5% SRM 88b	2.80	2.36	2.87	-
	92% NIST SRM 1d, 8% SRM 88b	4.10	3.51	4.27	-

Notes: NIST = National Institute of Standards and Technology, OTM = oxalate titration method, TGA = thermogravimetric analysis, XRF = X-ray fluorescence

Table 3. Mean $MgCO_3$ test results. Source: B&W

Overall, XRF provided accurate estimation of the total magnesium carbonate content for these samples, but it could not provide an indication of mineralogical phase. TGA results provided an acceptable estimation of dolomitic $MgCO_3$ content. Additional development of TGA would be required for quantification of the magnesium in magnesian calcite.

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$MgCO_3$ content of a given limestone is to determine the available $CaCO_3$. Available $CaCO_3$ is the amount of $CaCO_3$ within a limestone expected to react within a WFGD scrubber.

Total available calcium carbonate is calculated by subtracting the dolomitic carbonate contribution from the total carbonate of a sample. Total available $CaCO_3$ is calculated from TGA results by subtracting one molecule of $CaCO_3$ for every molecule of dolomitic $MgCO_3$ measured. Because magnesian calcite is credited toward total $CaCO_3$, this alkalinity would be credited toward total available alkalinity. In contrast, indication of mineral phase partitioning is beyond the capability of elemental analysis. Therefore, the convention is to assume that all the magnesium exists entirely as dolomite, $((Ca,Mg)(CO_3)_2)$, with a 1:1 ratio of $CaCO_3$ and $MgCO_3$. This fundamental difference is important to recognize but may not be significant due to the low concentrations of nondolomitic magnesium carbonate in many WFGD reagent limestones.

Analyses of filtrates from WFGD slurry samples indicate that dissolved magnesium concentrations range from several hundred to several thousand parts per million. The concentration is very dependent on the chloride content of the coal and the chloride concentration maintained by the purge stream. However, it is apparent from this data that considerable $MgCO_3$ is dissolved in WFGD systems. In some cases, utilities will provide a value for $MgCO_3$ utilization; typical values range from 20% to 35%. Research and development projects aimed at developing a correlation for predicting the available $MgCO_3$ are in progress.

TGA and XRF provide excellent agreement with expected values for total available $CaCO_3$ (Table 4). TGA results were slightly higher for most samples than XRF or the NIST-certified values. Much of this deviation may be attributed to the magnesium credited toward available alkalinity by the TGA method.

TGA did provide an overestimate of the total available $CaCO_3$ in NIST SRM 88b. This deviation could be due to assignment of some of the total $MgCO_3$ toward the total alkalinity, or the bias in total CO_2 evolved observed for this sample. Both TGA and XRF are acceptable for determination of the total available $CaCO_3$ in limestones used for WFGD.

Limestone Reactivity Testing

Determination of limestone reactivity is essential for accurate modeling and design of WFGD systems. Because reactivity is a measure of the rate at which a limestone will provide alkalinity to react with the acid created during SO_2 dissolution and hydrolysis, it is used in estimating the amount of limestone that must be fed into the absorber to maintain a given pH for a particular Ca/S stoichiometry and solids residence time. This data can then be used in the initial design of the WFGD system.

However, when a limestone possessing lower than design reactivity is used, feed rates would increase over those developed for the reactive limestone in order to maintain pH and SO_2 removal. As a result, gypsum purity would decrease due to increased inerts and unreacted $CaCO_3$ and $MgCO_3$ fed to the dewatering system. The flow rates of waste streams may also increase.

Currently, an industry standard for reactivity is not available, and a number of different procedures exist for conducting reactivity measurements. A test method is under development by ASTM; Babcock & Wilcox (B&W), utilities, limestone suppliers, and other original equipment manufacturers are supporting this effort by

limestone reactivity analysis:

- *Sample preparation.* Repeatable sample preparation is essential, as differences in limestone grind will produce different initial particle size distributions (PSD).

- *PH and automatic titrator control settings.* Tight system control should be employed to ensure constant pH and controlled acid addition. Undershoot and overshoot of pH are to be minimized because swings in pH will change the reaction rate, rendering results inconclusive.

- *Acid.* Because direct reaction between limestone and the anion species does not occur once the acid has dissociated, hydrochloric acid (HCl) may be used for limestone titration. The resulting products remain soluble, leaving unreacted limestone and inert species as the only particulates within the solution. When sulfuric acid (H_2SO_4) is used as the titrant, gypsum product is produced, precluding measurement of limestone PSD after the start of reaction and leading to the potential for electrode scaling and fouling.

- *Common ion concentration.* Due to the principles of chemical equilibrium, the rate of the reaction is affected by the relative concentrations of products and reactants within solution.

- *Wetting agent.* Use of a wetting agent ensures that all of the sample surface area is available for heterogeneous reaction. Ideally, the wetting agent also acts as a dispersant, reducing error potential from sample agglomeration.

- *Correction for initial PSD.* B&W has tested the same limestone that has been ground to different degrees of fineness. Results indicate that the empirically determined value for the reaction rate will not be constant unless it is corrected for PSD.

Reactivity Testing Methodology

The B&W limestone reactivity test method is used to ascertain the rate constant of a limestone sample and to qualify candidate limestones for suitability as WFGD reagents with regard to this parameter. This method uses an automatic titrator to add HCl to a fixed amount of limestone sample. The automatic titrator includes an agitator and provides precise control over the titration, which is necessary when determining the rate of reaction. PSD measurements are taken to provide an estimate of the limestone surface area available for reaction. Titration results and PSD measurements are used to estimate the reactivity constant of a given limestone. Results are compared to a limestone of known field performance.

To prepare the sample, the limestone is pulverized in a disk mill and screened such that 100% passes through 325 mesh. By using a constant mill setting during grinding, and by screening the sample, some control over PSD is afforded. However, obtaining two samples with the same PSD is highly unlikely, even from the same screening. This is primarily due to differences in the Bond Work Index of the different limestone samples. Double screening is not used due to concern that error may be induced through such activity as, theoretically, fractions of differing composition may result above and below the smallest screen.

subsequent hydrolysis in water. Because limestone does not react directly with SO_2 but, rather, reacts with the protons released from its absorption, any acid may be used to model the reaction of limestone and acid. B&W chooses to use HCl for limestone reactivity testing because the products of this reaction remain soluble in water, affording PSD measurements at later stages in the reaction.

A 1-gram sample of the prepared limestone is titrated with HCl in an automatic titrator until complete reaction at a pH of 3.85. Use of a compatible wetting agent is critical to allow wetting of the limestone sample and to ensure complete dispersion of the limestone sample particles. The volume of acid added is recorded, and this result is used to determine total alkalinity of the limestone sample. From analysis of the titration results, the amount of HCl required to titrate 60% of the total alkalinity is calculated.

A second 1-gram sample from the same screening is prepared and titrated at a pH of 5.0 until the calculated volume of acid required to react 60% of the total alkalinity has been added. Results are recorded as volume of acid added as a function of time (Figure 3).
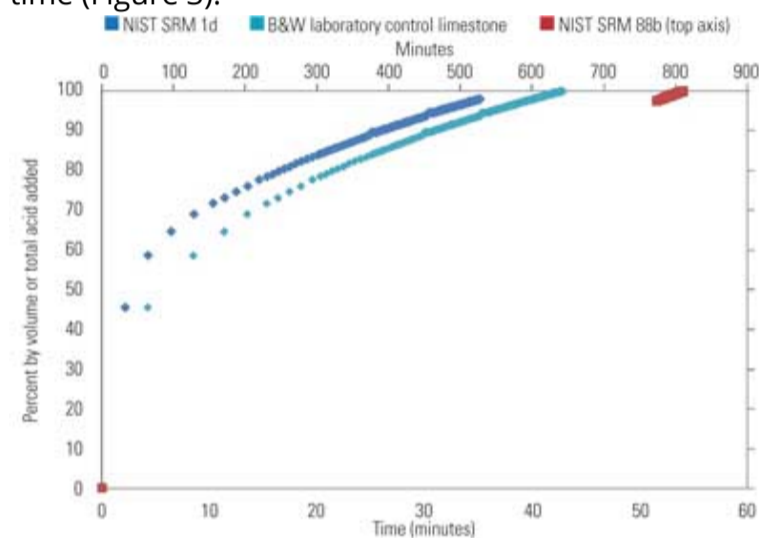
3.   Volume of acid added vs. time for 60% titration of a limestone's alkalinity. The NIST SRM 88b sample data uses the secondary axis time scale located on top. Source: B&W
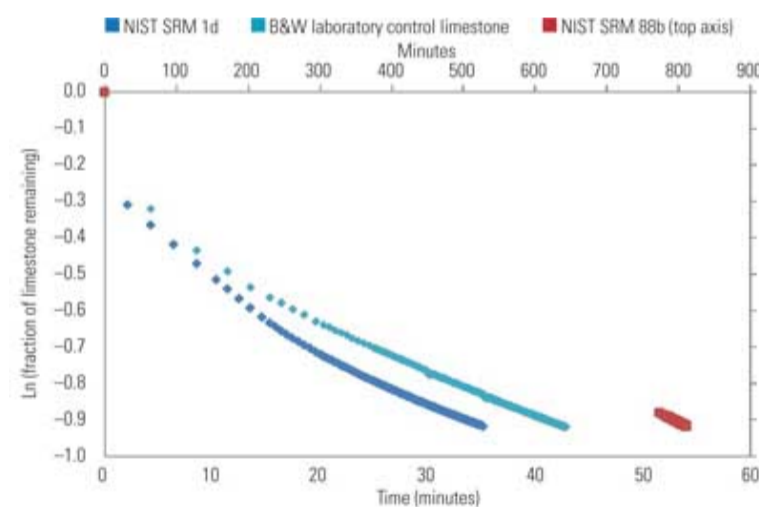
4.   Natural log of the fraction of limestone remaining vs. time. The NIST SRM 88b sample data uses the secondary axis time scale located on top. Source: B&W

During data analysis, the 60% titration data, original sample mass, and total alkalinity of the sample are used to construct a curve for the natural log of the limestone fraction remaining as a function of time (Figure 4). The derivative of this curve at the endpoint of titration is used in calculation of the reaction rate constant. PSD measurements for the sample are obtained at the titration endpoint to correspond with this slope.

A PSD reading is then taken on an aliquot of titrated sample. The initial and inert PSDs are also measured. The PSD readings are used to determine the specific surface area, expressed as the Sauter mean diameter (SMD), of the alkaline species in the sample at the titration endpoint. The alkaline particles are

microns of alkaline particles reacted per minute. The rate constant is independent of the actual particle size.

The B&W laboratory control limestone is a WFGD reagent limestone of known field performance, and this stone reacted in a similar period of time to NIST SRM 1d. In stark contrast, the dolomitic control limestone required almost 14 hours to reach 60% reaction at a pH of 5.0. Such a limestone is not suitable for use in WFGD systems.

Reactivity results for these limestones, and for reagent grade $CaCO_3$ normalized to the B&W control limestone, are provided in Table 5. Large variances in reactivity between the control stone, argillaceous limestone, and reagent grade $CaCO_3$ are thought to be attributed to differences in initial particle size distribution and sample preparation methods, as all of these should provide adequate performance in a WFGD system. Observe that the dolomitic limestone only exhibited 1% of the reactivity of the B&W control limestone, indicating that it would be unreactive in most WFGD systems.

Sample	Reactivity (%), normalized to B&W control limestone
B&W control limestone	100
Reagent grade $CaCO_3$	153
Argillaceous limestone (NIST SRM 1d)	61
Dolomitic limestone (NIST SRM 88b)	1

Table 5.   Relative reactivity of various limestones. Source: B&W

Testing to improve this method continues, with a primary focus on developing a correlation for initial particle size distribution. Preliminary results for the relative reactivity of samples of the same limestone ground to three different particle size distributions indicate that initial PSD may have significant impact on the reaction rate constant, as empirically determined from typical acid titration based reactivity methods.

XRF results provided by Don Broton, senior scientist of CTL Group Inc.

Normal
0
0
1
29
170
1
1
208
11.0

0

0
0

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ORP as a Predictor of WFGD Chemistry and Wastewater Treatment

Recent studies have shown that system oxidation-reduction potential (ORP) is not only an important factor for predicting wet flue gas desulfurization (WFGD) absorber chemistry but also may be a predictor of process equipment corrosion and wastewater treatment requirements.

Purge streams of wet flue gas desulfurization (WFGD) units, which are one byproduct of controlling SO_2 emissions from coal combustion, are being increasingly subjected to stricter wastewater regulations. Consequently, coal-fired power generators need a method for controlling the operational chemistry of these WFGD units. Upon implementation of a suitable control method, WFGD bleed stream chemistry and flow rate may be optimized, thereby resulting in improved performance of one or more downstream unit operations. A further benefit is reduced reagent and additive costs in various devicies, including the WFGD unit.

One control parameter of interest is the oxidation-reduction potential (ORP) of the bleed stream. Much like pH, the measurement of ORP can be taken in real time and integrated with other plant-monitoring data. By incorporating ORP measurements into a process control scheme for limestone forced-oxidized WFGD absorbers—along with various other control variables such as SO_2 removal, absorber pH, reagent flow rate and/or one or more reaction stoichiometries, and/or gypsum purity—generators are able to manage the oxidation states of various dissolved metals in the slurry and the potential reemission of mercury. (Also see "How to Measure Corrosion Processes Faster and More Accurately," May 2009 in the *POWER* archives and "Mercury Control: Capturing Mercury in Wet Scrubbers, Parts I and II," July and September 2007, respectively, in the *COAL POWER* archives—both available at powermag.com.)

A further benefit is control of the corrosion rate of the absorber recirculation tank (ART) and other alloy parts within the system. Many utilities have had ORP excursion events in WFGD wastewater discharge where the ORP readings changed from 150 millivolts (mV) to 300 mV to a reading above 500 mV. Previously, these fluctuations have gone largely unexplained. We have determined that this magnitude of change in ORP, in an ART, due to coal composition and upstream air quality control system (AQCS) effects on WFGD absorber chemistry, can accelerate corrosion.

One potential solution to fluctuating ORP readings is to use integrated process controls designed to tune the upstream operation of the AQCS train to produce consistent inlet flow parameters to the WFGD tower, rather than operating each as an independent process. The control of the ORP level in a WFGD system may produce improved plant operations by reducing the amount of wastewater treatment necessary and helping mitigate mercury reemission.

Fundamentals of ORP

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measured by an ORP probe in units of millivolts, which can be measured in real time under online plant process conditions. Positive readings are indicative of a system operating in oxidizing conditions; negative readings indicate a system operating in reducing conditions. If a material comes into contact with a solution that has a higher oxidative potential, then a chemical reaction may occur in which the solution is reduced and the material is oxidized.

The ORP of WFGD slurry and effluent is driven by the presence or absence of strong oxidizers. Many WFGD units operate at a moderate ORP range of about 100 mV to 300 mV, thereby achieving, or yielding, a rather stable voltage reading over time. The range of 100 mV to 300 mV is referred to as "low" ORP in this article. Such WFGD units often have oxidizer concentrations within the slurry below 200 ppm. Other WFGD units operate at higher ORP values, often above 500 mV. Slurries with high ORP almost always contain a high concentration of at least one strong oxidizer such as persulfate ($S_2O_8^{-2}$), peroxymonosulfate (HSO_5^-), or hypochlorite (OCl^-).

Persulfate has been identified and quantified using ion chromatography on absorber slurry samples collected at several sites. This anion is the most powerful oxidant of the peroxygen family of compounds, and it becomes a more effective oxidizer at scrubber process temperatures above about 120F due to free radical formation. In several instances, strong oxidizers were measured at total residual concentrations over 1,000 ppm in WFGD absorber slurry samples exhibiting high ORP after the samples were removed from the system and analyzed in the laboratory. Operating WFGD units are observed to swing from one process condition to the other (high to low ORP), but few, if any, hold at an intermediate value for an extended period of time. The rate and magnitude of these changes in slurry chemistry are indicative of upstream process changes affecting absorber chemistry.

Once you determine the WFGD slurry ORP, you can predict the dominant oxidation state for the various constituents that may be present in the absorber slurry. For many metals, solubility is a function of the oxidation state. Therefore, once the ORP of a solution has been determined, a prediction can be made of the preferred oxidation state for a given chemical species in a solution. The predominant species of various metals, and other compounds or ions, can thus be determined. Using this knowledge, the ORP in WFGD slurry can then be controlled in order to control the speciation of various metal ions, as well as other compounds and ions.

The range of potential electrochemical states of a given material can be found within a Pourbaix diagram for a given chemical species and presented as a function of pH and electrochemical potential versus pH. For example, a variety of general predictions about the various phases of mercury, selenium, and manganese based upon ORP and pH can be made (see the table).

| ORP Level	Mercury	Selenium	Manganese
<0 (mV)	Vapor	Selenite	Aqueous ion
0-300 mV	Aqueous ion, with the solids	Selenite	Aqueous ion
300-500 mV	Aqueous ion, with the solids	Selenate	Aqueous ion
>500 mV	Aqueous ion, with the solids	Selenate	MnO_2 solid

Dominant forms of mercury, selenium, and manganese for approximate ORP levels. *Source: Babcock & Wilcox Power Generation Group Inc.*

Dynamic Chemical Processes

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determined. Estimations of various parameters of WFGD absorber chemistry can also be determined, including the dominant oxidation states and phases of metals within the slurry, the potential reemission of mercury, and the risk of accelerated corrosion of the alloy vessel. Measurement of the system ORP also alerts operators to the likelihood of problems in downstream wastewater treatment (WWT) systems, especially the ratio and concentration of selenate ions to selenite ions within an effluent stream.

The chemistry inside a WFGD absorber is a complex system of hundreds of potentially changing ionic species and distinct compounds existing simultaneously throughout the slurry. The modeling of WFGD absorber slurries has been based on equilibrium thermodynamics to date. However, we have determined that in operating units, WFGD absorber slurry chemistry is more likely to be kinetically controlled. Most absorbers are operating at an unsteady state. Due to kinetic interaction, mercury could become reduced to the elemental state, thereby becoming vaporous and exiting the system boundaries in what is called mercury re-emission.

Another important aspect of ORP with relation to WFGD process chemistry is the reaction of any of the one or more strong oxidizers present with one or more halide ions present in solution, thereby resulting in increased demand for reagent in the absorber and a possible lowering of pH in the purge stream after the solids have been removed. Because persulfate is a powerful oxidant, it has the ability to convert some halide anions to their respective elemental state. Specifically, some chloride may convert to chlorine under high-ORP conditions:

$$2Cl^- + S_2O_8^{2-} \rightarrow Cl_2 + 2SO_4^{2-}$$
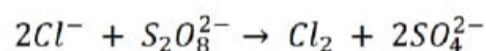
Similar reactions occur between the oxidizer(s) and other halide species present (for example, bromide, iodide, and the like). Thus, the concentration of chlorine in absorber slurry is present as three species in equilibrium within the aqueous phase: dissolved gas (Cl_2), hypochlorous acid, and ionic hypochlorite:

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^- \rightleftarrows 2H^+ + Cl^- + OCl^-$$
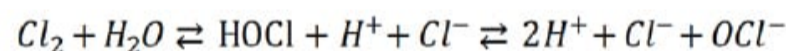
Within the typical WFGD operating range, equilibrium favors HOCl. The formation of H^+ ions associated with this chemical reaction will cause a decrease in pH as halogen-containing species are liberated from the scrubber. In WFGD systems that are operating in pH control mode, the reagent feed controls will respond to the lower pH by adding more reagent. In systems with high ORP levels, gypsum formation may occur without the addition of oxidation air when sulfite reacts with strong oxygen containing oxidizing agents. Higher gypsum purity can result as excess limestone, normally an impurity within the gypsum product, is reacted to buffer the system from dropping pH.

Due to the electro-reactive nature of mercury, ORP levels are a main driver in controlling reemission, dissolution into the slurry, and solid phase retention. Higher ORP values in the ART are favored in order to maintain dissolved mercury. ORP levels above 500 mV often favor an increase in the dissolved mercury, with constant total mercury content in the slurry. A decrease in the ORP in an ART is an indication of a less-oxidizing environment, leading to elemental mercury formation and potentially release (or reemission). A possible chemical pathway for mercury reemission to occur is shown in Equation 3:

$$Hg^{2+} + HSO_3^- + H_2O \rightarrow Hg^0 \uparrow + SO_4^{2-} + 3H^+$$
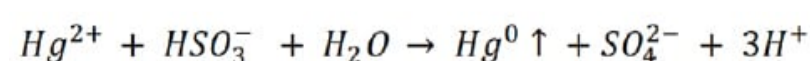
Swings in ORP value may also cause mercury to enter the elemental state and be reemitted from a WFGD tower.

WWT systems are tuned to control metals present in influents and to produce effluents within a certain concentration range. Changes in the influx of these metals to WWT may disrupt performance if controls and operational parameters cannot respond quickly. As swings in WFGD and/or WWT process occur, ORP may ultimately produce changes in the dominant state of regulated metals, thus permitting the WFGD effluent flow rate to affect the mass flux of each species. In this situation, detrimental fluctuations in ORP may result in minimal removal of some metals and potentially result in out-of-compliance operation.

Controlling process ORP can lead to improved efficiency of WWT systems related to selenium removal. WFGD effluent ORP controls the precipitation of many regulated metals, particularly selenium. At low ORP, selenium exists mainly as selenite (SeO_3^{-2}) and can be removed by many WWT methods including chemical precipitation. At higher ORP levels (greater than about 300 mV,) selenium will predominantly occur as selenate (SeO_4^{-2}), which passes through many WWT systems.

The combined effects of over 1,000 ppm of total oxidizers and low pH potentially associated with high-ORP WFGD effluent streams can result in damage to bioreactor stock and/or increased reagent costs in WWT systems. Strong oxidizers present within WFGD effluent have the potential to upset biological processes. During high-ORP conditions, the WFGD would essentially be feeding bleach (hypochlorite), peroxide, and stronger oxidizers to downstream systems; such oxidizers can damage microbial health when fed to biological treatment units.

Furthermore, high ORP in a WFGD effluent can result in low pH of WWT influent. As described earlier, oxidizers will continue to react with halide ions in solution, thereby liberating a hydronium ion and thus lowering pH. When excess carbonate is available, it may buffer such impacts. Once unreacted limestone is removed from the slurry filtrate during dewatering, the pH buffering capacity of the system rapidly decreases while oxidizer and halide ion concentrations remain and are fed to WWT.

Materials Must Resist Corrosion

Materials coming into contact with WFGD slurry and effluent should be selected with careful consideration to the corrosive potential of high-ORP slurries containing ionic manganese. Strong oxidative content is present in high-ORP slurry leaving the scrubber, and very low pH levels may be seen downstream in conjunction with high ORP. While industry focus has been given to WFGD ART corrosion, the potential exists for similar corrosion to occur in process pumps, dewatering operations, vacuum systems for gypsum production, as well as in process piping and WWT equipment.

Alloy 2205 duplex stainless steel (UNS S32205) is proving susceptible to accelerated corrosion from slurries that contain precipitated, or non-solubilized, manganese species and/or high ORP levels. Within the WFGD absorber, the majority of the corrosive attack is observed below the slurry level in the ART. Under high-ORP conditions, the rate of corrosion can accelerate. When the ORP of operating WFGD slurries is pushed above about 500 mV, manganese normally soluble as ionic Mn^{+2} will oxidize and precipitate out as MnO_2. When this precipitate contacts metal as part of a deposit, it serves as a galvanic cathode to exacerbate the fluoride and chloride driven under-deposit corrosion mechanism. Corrosion thus accelerated by manganese precipitation can be rapid and severe.

276) has been performed in some installations. Some plastics and resins may also be susceptible to attack from high ORP levels. Strong oxidizers within the slurry effluent may react with and thereby degrade some polymer bonds, because high-ORP filtrate samples were observed to weaken and discolor HDPE bottles in a laboratory setting. Within substances such as fiberglass-reinforced plastic, such a reaction with resins could potentially cause some dissolution of the resin and/or lead to fiber delamination.

Plantwide Impact

The WFGD ART ORP and the WWT influent process ORP both need to be controlled. Currently, studies are being performed to define techniques to maintain steady ORP and to allow for greater fuel flexibility. Such control would afford utilities the option to obtain the most cost-effective fuel, maintain a constant effluent for wastewater, and provide a better treatment scheme. Coal yard and boiler operators will need to work in conjunction with the plant's continuous emission monitoring systems, the WFGD system, and WWT plant operators to implement improvements that integrate the entire process. Learning how a parameter change upstream affects the WFGD and WWT systems is quickly becoming crucial. With full control of the AQCS process train and dewatering systems, control of WWT influent is expected.

The effects of blending coals, staging combustion, and swinging load can create issues with AQCS equipment, especially in environments where WFGD units are employed. The WFGD system serves as the catch basin for all flue gas byproducts as well as any fine ash not captured in an electrostatic precipitator or pulse jet fabric filter. Undesired ORP levels, or undesired fluctuations therein, can cause problems ranging from mercury reemission to increased corrosion and improper treatment of WFGD effluent. Adjustments to combustion processes may affect operating parameters of the WFGD environment as well as the WWT systems. Combustion systems need tuning to allow for efficient power generation, compliance with existing regulations, and flexibility to comply with anticipated, tighter water and solid discharge regulations.

Due to the potential for aggressive or accelerated corrosion of some alloy material in high-ORP environments, care should be taken on selection of alloys or materials in the WFGD slurry and filtrate contact zones. Constituents of the WFGD slurry will include limestone, gypsum, halide ions, and metals from the burned coal as well as silica from the ash and other up-stream constituents. The ORP levels in the tank can cause the metals to undergo phase partitioning or to change their solubility due to changes in their oxidation state.

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