DEVELOPMENT OF FIRESIDE CORROSION MODELS FOR ADVANCED COMBUSTION SYSTEMS

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ABSTRACT

A comprehensive fireside corrosion project was undertaken to better understand the corrosion mechanisms operating on the lower furnace walls and superheaters/reheaters in modern coal-fired utility boilers. Eight U.S. coals commonly burned in boilers are being selected to represent a wide range of coal chemistry. Subsequently, these coals will be fired in a pilot-scale combustion facility to closely simulate the actual conditions of staged combustion in the utility boilers. During the combustion testing, in-situ gas and deposit samples will be collected and analyzed via infurnace probing for each of the eight coals at selected waterwall and superheater/reheater locations. Such efforts will allow better characterization of the realistic combustion environments and corrosion products existing in the boilers. Once the conditions are defined, a series of long-term laboratory corrosion tests, each for 1000 hours, will be performed. These fireside corrosion tests will involve exposure of a total of eleven alloys and weld overlays, representing a wide range of compositions, to the laboratory conditions that resemble the actual boiler combustion environments. As a result of the laboratory testing, a fireside corrosion database will be generated for the subsequent corrosion modeling efforts. It is anticipated that results of the modeling will produce two predictive equations, one for the waterwalls in the lower furnace and one for the superheaters/reheaters in the upper furnace, which can be used to estimate the fireside corrosion rates of boiler tubes as a function of several key variables (e.g., sulfur, chlorine, alkali, alkaline, ash, pyrite, metal temperature, etc.). Applications of these predictive equations are expected to be versatile for both conventional and advanced combustion systems and not specific to any coals.

INTRODUCTION

The recent development of high-efficiency and low-emission coal-fired utility boilers has led to the demand for higher steam temperature and pressure conditions. The design strategies often involve implementation of staged combustion that produces corrosive combustion products in the lower furnace and the requirements for use of high-strength corrosion-resistant superheater/reheater alloys in the upper furnace. Examples include recent development of the ultra supercritical (USC) and oxy-coal combustion systems that will push the steam outlet temperatures up to 760°C (1400°F) and steam pressures up to 35 MPa (5000 psi).¹ While higher efficiencies and lower emissions can be

realized from these advanced combustion systems, accelerated fireside corrosion is also expected to occur on the boiler tubes. For instance, low-NO_X combustion produces H₂S in the flue gas and FeS in the deposit due to incomplete combustion of the sulfur-bearing species in coal. Both of these sulfides are known to increase fireside corrosion on the waterwalls via sulfidation, although the corrosion mechanisms are distinctly different.^{2,3} Utility boilers retrofitted with low-NO_X burners and NOx ports in recent years have indeed experienced accelerated tube wastage in the lower furnace. Consequently, application of coatings and weld overlays is often employed on the lower furnace walls to impede the corrosion wastage. In the upper furnace, higher steam temperatures and pressures inevitably raise the metal temperatures of superheaters and reheaters, thus increasing the tendency for coal ash corrosion attack.

While the boiler operating conditions are important variables, the coal chemistry also plays a vital role in fireside corrosion. Some impurity constituents of coal are well known to accelerate corrosion wastage. For example, high sulfur and chlorine contents in the coal have long been recognized as a major cause for boiler tube corrosion on both the waterwall and superheater/reheater surfaces. The effects of other constituents on corrosion, such as the alkali and alkaline metal concentrations as well as the total ash content, are also important but less understood. Indeed, operating experiences indicate that the corrosivity of coal is not just determined by individual impurities. Rather, it is the result of complex, synergistic effects of all these impurity constituents interacting simultaneously. There were attempts in the past to link coal corrosivity to its impurities based on empirical correlation and indexing. However, the results proved to be unreliable and often coal-specific due to oversimplification of the interactions and/or significant variations in coal chemistry from seam to seam and mine to mine.

Therefore, it is the objective of this three-year project to develop comprehensive corrosion models that can be used to reliably predict the corrosion rates of boiler tubes under staged combustion conditions in the lower furnace and coal ash corrosion conditions in the upper furnace. To accomplish this goal, B&W will down-select eight common U.S. coals that represent a wide range of coal compositions burned in modern utility boilers. These coals will then be combusted in a pilot-scale combustion facility to closely simulate the actual staged combustion encountered in the utility boilers. During the combustion testing, in-situ gas and deposit samples will be obtained and analyzed for each coal at the selected waterwall and superheater locations. Such efforts will allow B&W to better define the realistic combustion environments and corrosive products present in the boilers. Once the conditions are determined, a series of long-term laboratory corrosion tests, 1000 hours each, will be performed. These corrosion tests will expose different alloys and coatings in a wide range of alloy compositions to the laboratory conditions simulating the actual boiler environments. As a result of the laboratory tests, a fireside corrosion database will be generated and used for the subsequent corrosion modeling efforts. It is anticipated that the modeling efforts will lead to two predictive equations, one for the lower furnace walls and one for superheaters/reheaters, that can be used to estimate the corrosion rates of boiler tubes as a function of key variables, such as sulfur, chlorine, alkali, alkaline, ash, FeS₂, metal temperature, gas temperature, etc. Application of these predictive equations is expected to be versatile for both conventional and advanced combustion systems and not specific to any particular coals.

EXPERIMENTAL PROCEDURES

B&W will select eight U.S. coals that represent a wide range of coal chemistry commonly burned in modern utility boilers. These coals will subsequently be combusted in a proven pilot-scale combustion facility, the Burner Flow Reactor (BFR), available at Brigham Young University. The BFR, rated at a 0.6 MBtu/hour heat input, is capable of burning pulverized coal to produce variable swirl flames that replicate the realistic burner flow dynamics in coal-fired utility boilers. The current project work scope is divided into six tasks, which are briefly described as follows.

Task 1 - Coal Selection, Procurement, and Handling

The purpose of this task is to select and procure coals that consist of a wide range of impurities relevant to fireside corrosion. B&W will review several coal databases and investigate the availability of commercial U.S. coals from coal vendors. Up to 24 coals will be initially selected and their typical analyses obtained from the coal databases, coal mines, and vendors. B&W will perform additional chemical analyses for impurities that are considered prevalent to fireside corrosion (e.g., pyretic sulfur and organic chloride) but unavailable from the databases. The coal chemistry will be carefully evaluated before the final selection for the subsequent combustion testing. Table 1 shows the typical properties of some U.S. coal families under consideration.

For this study, the coal selection processes will generally adhere to the following guidelines:

- Three eastern bituminous coals with various sulfur concentrations but comparable alkaline and chlorine contents B&W will look for three eastern bituminous coals with high, medium, and low sulfur, respectively, which are commonly burned in U.S. utility boilers. The pyretic to organic sulfur ratio will also be considered as a key parameter that may affect the coal corrosivity. Illinois #6 with more than 4% sulfur is a potential candidate for the high sulfur coal, and Pittsburgh #8 with approximately 2% sulfur is a candidate for the medium sulfur coal.
- A high-chlorine bituminous coal Eastern bituminous coals typically have a chlorine content of 500 to 1500 ppm. For the purpose of this corrosion study, an Illinois bituminous coal with a high chlorine content, i.e., >3000 ppm, will likely be chosen.
- An eastern bituminous coal with a high total alkali content (i.e., Na₂O and K₂O).
- A western subbituminous coal with a high total alkaline earth metal content (i.e., MgO & CaO) The Decker and Spring Creek PRB coals contain <0.5% sulfur and <10 ppm chlorine and are popular fuels for the U.S. power plants. These coals also contain higher levels of magnesium and calcium that are of interest to this study.
- A North Dakota lignite with a high ash and moisture contents.

	Anthracit	Pittsburgh #8 HV Bituminous	Illinois #6 HV Bituminous	Upper Freeport MV Bituminous	Spring Creek Subbitu- minous	Decker Subbitu- minous	Lignite	Lignite (S.Hallsville	Lignite) (Bryan)	Lignite (San Miguel
State		Ohio or Pa.	Illinois	Pennsylvania	Wyoming	Montana	North Dakota	Texas	Texas	Texas
Total Moisture	7.7	5.2	17.6	2.2	24.1	23.4	33.3	37.7	34.1	14.2
Proximate:										
Volatile matter, dry	6.4	40.2	44.2	28.1	43.1	40.8	43.6	45.2	31.5	21.2
Fixed carbon, dry	83.1	50.7	45.0	58.5	51.2	54.0	45.3	44.4	18.1	10.0
Ash, dry	10.5	9.1	10.8	13.4	5.7	5.2	11.1	10.4	50.4	68.8
Heating value, Btu/lb										
As-received	11,890	12,540	10,300	12,970	9,190	9,540	7,090	7.080	3,930	2,740
Dry	12,880	13,230	12,500	13,260	12,110	12,450	10,630	11,360	5,960	3,200
MAF	14,390	14,550	14,010	15,320	12,840	13,130	11,960	12,680	12,020	10,260
Ultimate:										
Carbon	83.7	74.0	69.0	74.9	70.3	72.0	63.3	66.3	33.8	18.4
Hydrogen	1.9	5.1	4.9	4.7	5.0	5.0	4.5	4.9	3.3	2.3
Nitrogen	0.9	1.6	1.0	1.27	0.96	0.95	1.0	1.0	0.4	0.29
Sulfur	0.7	2.3	4.3	0.76	0.35	0.44	1.1	1.2	1.0	1.2
Ash	10.5	9.1	10.8	13.4	5.7	5.2	11.1	10.4	50.4	68.8
Oxygen	2.3	7.9	10.0	4.97	17.69	16.41	19.0	16.2	11.1	9.01
Ash fusion temps, F										
Reducing/Oxidizing:	Rod Orid	Red Oxid	Red Oxid	Red Oxid	Red Oxid	Red Oxid	Red Oxid R	ed Oxid F	ted Oxid	Red Oxio
ID	neu Oxiu	2220 2560	1930 2140	2750+ 2750+	2100 2180	2120 2420			370 2470	2730 2750
ST Sp.		2440 2640	2040 2330	2750+ 2750+	2160 2300	2120 2420			580 2670	2750+ 275
ST Hsp.		2440 2650 2470 2650	2040 2330	2750+ 2750+	2100 2300	2250 2470 2270 2490			690 2760	2750+ 275
ST risp. FT 0.0625 in.		2570 2670	2420 2600	2750+ 2750+	2170 2320	2310 2490				· 2750+ 2750
FT 0.0625 m. FT Flat			2420 2600 2490 2700	2750+ 2750+	2190 2360 2370 2700			$320 \ 2350 \ 2350 \ 2350 \ 2400 \ 2400 \ 2400 \ 2400 \ 2400 \ 25$		· 2750+ 275 · 2750+ 275
FI Flat		2100+ 2100+	2490 2700	2700+ 2700+	2010 2100	2000 2100+	2300 2300 23	50 2400 2	900+ 2900+	2700+ 2700
Ash analysis:										
SiO_2	51.0	50.58	41.68	59.60	32.61	23.77	29.80	23.32	62.4	66.85
Al_2O_3	34.0	24.62	20.0	27.42	13.38	15.79	10.0	13.0	21.5	23.62
Fe_2O_3	3.5	17.16	19.0	4.67	7.53	6.41	9.0	22.0	3.0	1.18
TiO_2	2.4	1.10	0.8	1.34	1.57	1.08	0.4	0.8	0.5	1.46
CaO	0.6	1.13	8.0	0.62	15.12	21.85	19.0	22.0	3.0	1.76
MgO	0.3	0.62	0.8	0.75	4.26	3.11	5.0	5.0	1.2	0.42
Na ₂ O	0.74	0.39	1.62	0.42	7.41	6.20	5.80	1.05	0.59	1.67
$K_{2}O$	2.65	1.99	1.63	2.47	0.87	0.57	0.49	0.27	0.92	1.57
P_2O_5	-	0.39	-	0.42	0.44	0.99	-	-	-	-
SO ₃	1.38	1.11	4.41	0.99	14.56	18.85	20.85	9.08	3.50	1.32

Table 1 - Typical Properties of U.S. Coals

After the eight coals are selected from Task 1, the coal chemistry will be further confirmed by the following analyses:

- Proximate & Ultimate (including Btu) analysis
- Ash Analysis (Major Element)
- Grindability Index (HGI) determination.

Following the analysis, the coals will be procured, partially dried, and pulverized. The pulverizer and mill settings will be properly adjusted to produce the typical particle size distribution of 70% at <200 mesh as for modern coal-fired utility boilers.

Task 2 – BFR Pilot-Scale Combustion Testing

The objective of this task is to produce pertinent combustion gases and deposits in a pilot-scale combustion facility burning the coals selected from Task 1. Specifically, this task will generate the same flue gas compositions, gas temperatures, and deposit chemistry as in modern coal-fired utility boilers at the following furnace locations:

- Lower furnace sidewalls near the burner zone of coal-fired boilers where the most aggressive low-NO_x corrosion is typically experienced.
- Superheaters/reheaters in the upper furnace where the most severe coal ash corrosion is taking place.

As mentioned previously, the combustion testing will be performed in the BFR at Brigham Young University. Swirled flame will be implemented for the combustion tests to produce large gradients in temperature and stoichiometry in the burner zone. The facility will be modified to allow staged combustion of pulverized coals to simulate the conditions of lower furnace walls. In modern coal-fired utility boilers, the combustion is typically staged at 0.80-0.85. Excess air will be introduced through a NOx port downstream of the burner zone to create oxidizing combustion environments typical of the superheaters and reheaters for coal ash corrosion.

Task 3 – Gas and Deposit Sampling

The goal of this task is to identify the combustion products present at the lower furnace walls and superheater/reheater banks in the pilot-scale combustion facility discussed above for Task 2. In-situ gas and deposit sampling will be performed in the test facility using water-cooled probes. A Fourier transform infrared spectroscopy (FTIR) and gas chromatograph (GC), capable of detecting a wide range of gases at concentrations as low as 100 ppb, will be employed for online analysis of the flue gases during the combustion testing. The gas species of interest to this project include CO, CO₂, SO₂, SO₃, NO_x, H₂O, H₂S, O₂, HCl, and H₂.

Task 4 – Laboratory Corrosion Testing

This task will determine the wastage rates of selected boiler tube alloys and weld overlays by exposing them to the fireside conditions of lower and upper furnace. Mixed gases and ash deposits will be employed to closely simulate the combustion conditions existing on the furnace walls and superheaters/reheaters, as determined from burning each of the eight coals in the BFR for Tasks 2 and 3.

Two laboratory furnace systems dedicated to this study will be used to perform a series of 1000-hour corrosion tests. Figure 1 shows one of the two furnace facilities located in B&W's Fireside Corrosion Laboratory. Coupons of boiler tube materials of interest will be covered with simulated ash deposits, heated to desired temperatures, and exposed to mixed gases. A total of eleven alloys and weld overlays with a large variation in composition will be exposed to each of the coal ash corrosion conditions for superheaters/reheaters, and a different set of eleven materials will be selected for each of the reducing/sulfidizing conditions for waterwall tubes.

Duplicate samples of each material will be tested. One of the duplicate samples will be used for corrosion rate calculations. Therefore, these coupons will be carefully weighed and measured prior to the corrosion tests. After the exposure, the specimens will be chemically cleaned to remove the ash deposits as well as the corrosion products

formed on the metal surfaces. Subsequently, the weighs and dimensions of the cleaned samples will re-measured to determine the metal losses resulting from the long-term corrosion exposures. The weight and thickness losses will be used to calculate the corrosion rates on an annual basis.



Figure 1 – Two Fireside Corrosion Testing Facilities Dedicated to the Current Materials Project.

The second duplicate samples will be cross-sectioned, polished, and examined under a SEM/EDS to characterize the deposit and scale/metal interfaces. These metallographic samples will also be used to reveal any internal corrosion attack that is not readily detectable by the weight and thickness measurements.

Task 5 – Corrosion Model Development

Two fireside corrosion models will be developed from this project, one for the lower furnace walls in coal-fired utility boilers burning coal substoichiometrically and one for the superheaters/reheaters in the upper furnace. Because the corrosion mechanisms operating on the furnace walls and superheaters/reheaters are distinctly different, they must be considered separately. In the lower furnace, sulfidation dominates the corrosion mechanism due primarily to the staged combustion of coals. Stage combustion allows the formation of reduced sulfur-bearing species in the flue gas and deposit. These species attack the boiler tube surfaces by forming rapidly growing metal sulfides, such as FeS and NiS, instead of protective oxides. The lack of a protective oxide results in accelerated wastage of the furnace wall tubes. In addition, coals containing a high level of chlorine can induce chlorination, also known as active corrosion, that may further accelerate the wastage of boiler tubes.

On the other hand, coal ash corrosion operating on the superheaters and reheaters involves the formation of a thin layer of inorganic salts condensed on the boiler tube surfaces beneath the bulk of ash deposit. The salt layer, often referred to as the "white layer" observed under an optical microscope, consists primarily of mixed sulfates, such as $(Na,K)_2SO_4$ and $Fe_2(SO_4)_3$. The presence of multiple sulfate compounds can reduce the liquidus temperatures of the white layer to a level below the metal temperatures, thus allowing "hot corrosion" to take place. Hot corrosion is a special class of high-temperature corrosion that involves the presence of molten salts.⁴ Once molten, the salt can cause dissolution and breakdown of the otherwise protective oxide scales formed on the boiler tubes. The addition of chlorides to the white layer in boilers burning high-chlorine coals may further facilitate the alkali and chloride condensations as well as reduce the liquidus temperatures.

Based on current understanding of the fireside corrosion mechanisms, it becomes clear that the corrosion models under the development of this project must incorporate the concentrations of corrosive species in the combustion products (i.e., thermodynamics) and the transport of the corrosive species to the tube surfaces (i.e., kinetics). The concentrations of the corrosive species can sometimes be estimated based on full or partial equilibrium of the combustion gases. However, caution must be exercised when performing the thermodynamic calculations, as the combustion gas temperatures change rapidly from the burner zone to the surfaces of boiler tubes. Consequently, misleading results can be encountered if incorrect assumptions are made to the calculations.

With all the factors considered, the modeling effort for this study will commence immediately after generation of the fireside corrosion database from Task 4. This database will be carefully analyzed using the thermodynamic and kinetic principles. Statistical and regression analyses will be systematically performed to correlate the corrosion rates with the complex interactions of coal impurity constituents. When applicable, prior B&W corrosion data will also be incorporated. Once a better understanding of the corrosion mechanisms is accomplished, predictive equations will be formulated to link the corrosion rates of boiler tube alloys to coal impurities and boiler operations for the lower furnace walls and superheaters/reheaters, respectively.

Task 6 – Reporting

All technical and management reports will be submitted in accordance with the Federal Assistance Reporting Checklist and the instructions accompanying the checklist.

RESULTS AND DISCUSSION

This three-year corrosion project was officially kicked off in January 2008 and therefore is still in its early stages. Much of the effort to-date has been placed on Task 1 to identify and select eight U.S. coals pertinent to fireside corrosion modeling. Three coal databases have been explored for the coal selection, which include B&W Coal Database, Penn State Coal Database, and USGS Coal Database. Among them, information contained in the Penn State Coal Database is perhaps the most detailed and up to date. This database is also structured to be the most user-friendly for coal property search. For Task 1, several coals have been identified as candidates for each of the coal property groups discussed above for Task 1. For high sulfur bituminous coals, multiple choices are available. For example, the Ohio #5 coal seam has a sulfur content, on a dry basis, at as high as 9 wt.%. Specifically, the Empire mine (hvAb) contains a sulfur content at approximately 4 %, the East Fairfield County mine (hvAb) at 5 %, and the Holmes County (hvBb) mine at 6 %. In Kentucky, the Camp #1 mine (hvBb) of Kentucky #9 seam has a sulfur concentration at 4 %, Paradise mine (hvBb) of the Kentucky #11 seam at 5 %, and Homestead mine (hvCb) of the Kentucky #11 seam at 6%.

Since chlorine is an important coal property to this program, various chlorinebearing coals have been considered along with their sulfur contents. In Illinois, the Will Scarlett mine (hvAb) of Top Dekoven seam has a chlorine content of 0.27% and sulfur of 4.69% on a dry basis. Similarly, the Eagle #2 mine (hvAb) of Illinois #5 seam has 0.27% chlorine and 4.72% sulfur. Furthermore, the Orient #3 mine (hvBb) of Illinois #6 seam has a combination of lower sulfur content of 1.35% but higher chlorine of 0.45%. This coal is strong candidate for this study to single out the effect of chlorine on fireside corrosion.

For additional selection of medium-sulfur bituminous coals, the Hillsville mine (hvBb) of Middle Kittanning seam, which consists of 2.77 % sulfur and 0.16 % chlorine, and the O'Donnell #1 mine (hvAb) of Pittsburgh seam, which consists of 3.07 % sulfur and 0.06 % chlorine, look promising. The Stinson #3 mine (hvAb) of Elkhorn #3 seam having 0.98 % sulfur and 0.33 % chlorine may also be a good choice for this coal group.

In addition to individual impurities, the base/acid ratio (BAR) was also used as a starting parameter to identify bituminous coals that have a relatively high calcium and magnesium content in the ash. Several coals have been identified as candidates for this study. For example, the Stahlman mine (3500 Pit) (hvAb) of Clarion seam, with a BAR of 3.58, and the Bokoshe #10 mine (hvAb) of Upper Hartshorne seam, with a BAR of 7.0, are among the possibilities for coals with a high alkaline earth metal content. If necessary, there are bituminous coals, such as the Michigan #5 mine (hvCb) in Iowa, that contain an even higher BAR ratio at 12-78. Such a high BAR is attributed to an unusually high calcium concentration, i.e., 20-30%, in the ash. Typically, these coals also have a high sulfur contents, ranging from 9 to 10%, with pyretic sulfur being the main constituent at approximately 7 %.

For sub-bituminous coals, the Spring Creek mine (subB) in Montana has a sulfur content of 0.5 % and chlorine content of 0.07%. Similarly, the Black Thunder mine in Wyoming has a relatively low sulfur at 0.43% and a very low chlorine content. Both of these sub-bituminous mines are from the Powder River Basin (PRB). On the other hand, North Dakota lignite at the Beulah mine is a unique candidate for its high ash content at 9% and extremely high moisture content at approximately 30% as-received. This coal has a sulfur concentration of typically less than 1%.

Due to its unique characteristics and popularity, a Powder River Basin (PRB) coal, most likely a Wyoming coal from the Black Thunder mine, will be included in the test matrix as one of the eight coals. This PRB coal exhibits a very high Ca/S ratio, which has been postulated to be one of the probable reasons for accelerating fireside corrosion found in utility boilers implementing fuel blending. Therefore, this coal is of particular interest to this study. Final selection of the remaining coals is continued, with special considerations given to the various coal properties and impurity concentrations.

For Task 4, construction of the two furnace facilities in B&W's high-temperature corrosion laboratory is complete. One of the facilities is dedicated to coal ash corrosion under oxidizing combustion gases, and the other is to furnace wall corrosion under reducing/sulfidizing conditions. Both facilities are ready for long-term fireside corrosion testing.

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