

# **CORROSION EFFECTS OF CALCIUM CHLORIDE INJECTION FOR MERCURY CONTROL ON THE POLLUTION CONTROL EQUIPMENT**

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## ABSTRACT

In response to the Clean Air Mercury Rule (CAMR) of 2005, Black Hills Power (BHP) initiated testing of a calcium chloride ( $\text{CaCl}_2$ ) injection method in their Wygen 1 (Gillette, WY) coal-fired power plant to help lower mercury emissions. In 2006, Babcock & Wilcox (B&W) was contracted to test their  $\text{CaCl}_2$  technology *in-situ* by adding a  $\text{CaCl}_2$  solution onto the raw, pre-pulverized coal during normal operation of Wygen 1. Follow-up tests were conducted by BHP in 2007. Data were collected from these two time periods and analyzed by a collaborative investigation team from Western Research Institute (WRI) and the University of Wyoming (UW) to see if there were any effects on the current air pollution control systems. During a  $\text{CaCl}_2$  injection period in 2007, corrosion was monitored in the flue and recycle ash system by placing corrosion coupons in strategic locations to test if corrosion was enhanced by the  $\text{CaCl}_2$  injection. While the  $\text{CaCl}_2$  produced a reduction in stack mercury levels, there was some evidence of beneficial impacts on the removal of  $\text{SO}_2$  from the flue gas during  $\text{CaCl}_2$  injection. Data on  $\text{NO}_x$  remained inconclusive. It was also discovered that corrosion was enhanced significantly in the Spray Drier Absorber (SDA) vessel and corresponding outlet ductwork during  $\text{CaCl}_2$  injections. Further studies are being carried out in the field and lab to better understand the corrosive effects of  $\text{CaCl}_2$  to help formulate operation controls to manage the increased corrosion rates.

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## EXECUTIVE SUMMARY

The University of Wyoming (UW) and Western Research Institute (WRI) have been collaborating with the BHP/B&W team to support the testing of  $\text{CaCl}_2$  injection as a means to controlling power plant mercury emissions. The main objective of the work carried out under this task was to assess and quantify corrosion effects of chloride injection in the firebox and on the back-pass components of the power plant. Other objectives included quantification of the beneficial effects of the calcium chloride injection on the mercury,  $\text{SO}_2$  and  $\text{NO}_x$  emissions, multi-pollutant control benefits.

A series of corrosion racks were exposed in the BHP Wygen 1 Coal-fired power plant. Corrosion coupons exposed were evaluated for corrosion losses during normal coal operations and during coal operations with  $\text{CaCl}_2$  injection. In the most part the corrosion rates for carbon steel were quite low and manageable by routine plant design corrosion allowance. However, relative corrosion rates during chloride injection were indeed accelerated in and at the outlet of the Spray Drier Absorber.

Comparison of the flyash samples collected during the  $\text{CaCl}_2$  injection period contained nearly two times more mercury as those collected during no chloride injection; an obvious reflection of the fact that chloride injection indeed favorably affected the mercury speciation to allow better capture.

## INTRODUCTION AND BACKGROUND

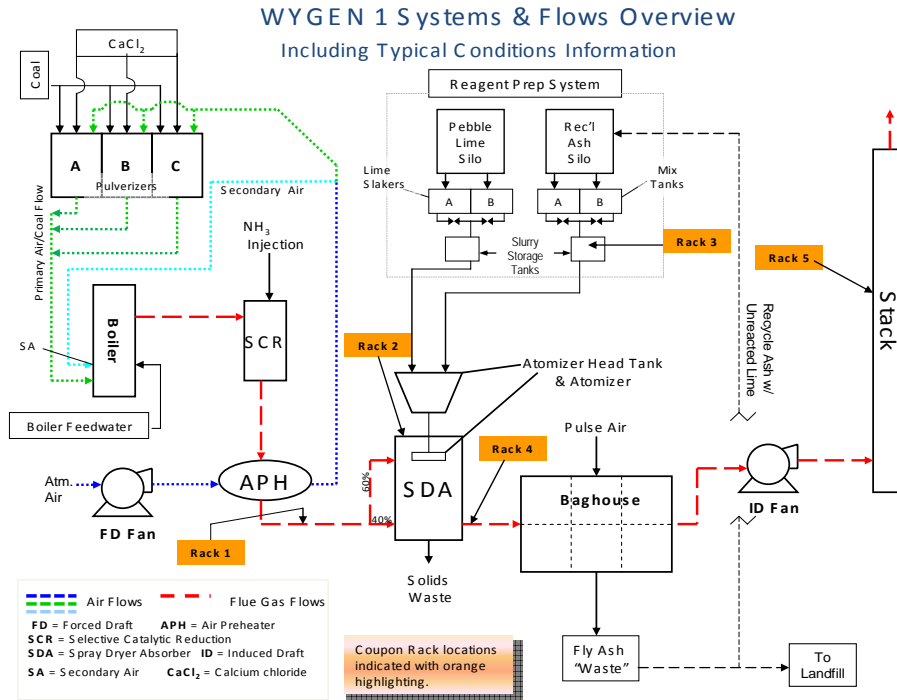
### Report of Mercury Reduction Technology Effects on Wygen 1

In March 2005, the United States Environmental Protection Agency (USEPA) issued the Clean Air Mercury Rule (CAMR), a cap and trade approach to controlling mercury (Hg) emissions from fossil fuel-fired power plants in the U.S. (Feeley *et al.*, 2005) This legislation prompted Black Hills Power (BHP) to seek economical and effective mercury control technology to add to the flue gas cleaning systems of their existing and future coal-fired power plants. Babcock & Wilcox (B&W) was contracted to test the effectiveness of their calcium chloride ( $\text{CaCl}_2$ ) injection method at the Wygen 1 power generation plant in Gillette, WY, where they ran a series of mercury control tests to determine the technology's effect on stack mercury emissions.

Wygen 1 is a 90 megawatt coal-fired power plant with three emissions control devices to scrub the flue gas to below Wyoming Department of Environmental Quality permit levels. Aside from having low- $\text{NO}_x$  technology burners, Wygen 1 employs ammonia injection in a Selective Catalytic Reducer (SCR) to ensure sufficient  $\text{NO}_x$  removal. The flue gas next enters a Spray Dyer Absorber (SDA), where a lime slurry aids in the removal of  $\text{SO}_2$ . The final step in cleaning the flue gas is in the baghouses. The baghouses aid in the removal of particulates from the flue gas by passing the flue gas through fabric filters ("bags").

Powder River Basin (PRB) coals, such as Wyodak (which fuels Wygen 1), are generally low in chloride. Some laboratory studies have indicated that corrosion of boiler tubes in a coal-fired power plant vary directly with flue gas chloride concentrations (Pan *et al.*, 2003). Studies by B&W show the benefit of higher chloride levels is enhanced mercury capture in the flue gas cleaning equipment at Wygen 1. The B&W mercury control technology artificially increases the chloride levels in the feed coal yielding a double benefit. In addition to test results at Wygen 1 showing this technology effectively reduces mercury emissions in the stack; it allows the chloride levels in the feed coal to be controlled for optimum performance.

Chlorides are added to the coal by injecting aqueous calcium chloride solution onto the pre-pulverized coal as it enters each of the pulverizers (Figure 1). The  $\text{CaCl}_2$  is mixed evenly with the coal via the pulverization process and carried with primary combustion air to the boiler's firebox burners. Mercury, found naturally in the coal, reacts with the abundance of chloride in the flue gas and is captured by the existing flue gas cleaning equipment (Pan *et al.*, 2003). This increase in chloride concentrations in the flue gas may possibly affect the corrosion rates within the plant, but may also affect the performance of the air pollution control equipment.



**Figure 1. System Overview of Wygen 1**

The University of Wyoming (UW) and Western Research Institute (WRI) have been collaborating with the BHP/B&W team to support the testing of this technology by identifying and quantifying:

1. corrosion effects associated with injecting CaCl<sub>2</sub> and
2. multi-pollutant control benefits.

## METHODS

### Corrosion Surveillance Methods

Corrosion coupons were placed in strategic locations during periods with and without CaCl<sub>2</sub> injection in the back-pass section of the plant downstream of the air preheater (Figure 1). Corrosion coupon racks were specifically designed for each location to accommodate installations into various types of ports and conditions. Six locations were originally planned. The baghouse outlet head space could not be safely accessed to install a coupon rack. The locations in which corrosion racks were successfully placed include:

- a. Air Preheater Outlet (APH-OUT) ductwork between the preheater and the Spray Dryer Absorber (SDA)
- b. Roof of Spray Dryer Absorber (SDA Roof) near the wall of the vessel



- c. Spray Dryer Absorber Outlet (SDA-OUT) ductwork
- d. Submerged in the slurry of the Recycle Ash Slurry Tank (RAST) and
- e. In the stack (Stack) by the continuous emission monitors (CEMs)

### **Rough cut coupon assembly on coupon rack**

The first part of each coupon rack consisted of three 2" (nominal) coupons made in-house at Wygen 1 from 0.125"-thick flat bar stock carbon steel used in plant repairs. These were placed on 0.5" all-thread stock of varying lengths to insure coupons' exposure to the flue gas stream (see Appendix A for rack design specs). Assembly of this portion of each coupon rack can be viewed in Pictures 1&3.

The rough cut coupons were formed by using an oxy-acetylene cutting torch to cut rounds out of the bar stock and a bench grinder was employed to take off the slag left by the cutting process. The center hole was drilled with a 0.625" drill bit. They were weighed in triplicate to the nearest 0.1 gram just prior to installation.

A 0.5" nut was placed about 3.5" up a section of all-thread, followed by a rubber washer hand-cut from a 0.125"-thick sheet. The coupon was placed against the rubber washer with a 0.625" outer-diameter rubber o-ring fit snugly and flush in the center hole of the coupon. Another hand-cut rubber washer was placed against the coupon's opposite face. The two hand-cut rubber washers and the o-ring in the center hole of the coupon provided electrical isolation for the specimen during exposure. This pattern was repeated for two additional coupons on each rack for a total of three handmade coupons per rack. The 0.5" nuts (0.5" wide) and the two hand-cut rubber washers between each corrosion coupon provided 0.75" of space between the coupons. A final 0.5" nut was placed on the terminal end of each rack to hold the assembly in place, tightened just enough to prevent free rotation of the coupons around the all-thread.

### **Metal Samples, Inc. coupon assembly and attachment to coupon rack**

To gain accurate and reliable data on corrosion losses, three standardized coupons from Metal Samples, Inc. (MSI) were placed on an adapter piece and added to the terminal end of the rough cut coupons' all-thread for each location. These 1.25"-diameter coupons were made of C1018 mild carbon steel alloy, 0.125" thick with a center hole of 0.270". A chamfer around the center hole extends out to 0.5" in diameter on one side of the coupon. At MSI, the coupons were each pre-weighed to the nearest 0.0001g, sequenced with a stamped number and had a sand-blasted finish.

The adapter piece was made by WRI personnel by arc-welding a 7" piece of 0.25" all-thread into a 0.5" coupling nut (see Pictures 1&2), leaving 6" of all-thread length for coupon installation. The mounting of the coupons were similar to that of the hand-made coupons

mentioned above. A 0.25" nut was threaded onto the all-thread 4" away from the 0.5" coupling nut followed by a 0.5"-diameter, 0.063"-thick Teflon washer. PTFE pipe thread tape was "balled up" around the all-thread after the Teflon washer enough to allow the MSI coupon to sit firmly on the 0.25" all-thread. The corrosion coupon was then set in place on the PTFE tape followed by a 0.625"-diameter, 0.25"-thick Teflon spacer, giving the 1.25" coupons a 0.25" space between them. This style of spacer was placed on each side of the middle coupon, with another 0.5" washer placed on the terminal face of the last coupon before the 0.25" nut. The Teflon washers and spacers and PTFE tape provided the electrical isolation for each corrosion specimen. Again, the two 0.25" nuts were tightened just enough to prevent the coupons from freely rotating around the all-thread during the exposure period. The entire adapter assembly was attached to the terminal end of the 0.5" all-thread against the last 0.5" nut with a 0.5" lock-washer to guard against being loosened.

Finally, the corrosion coupon rack was prepared for installation by attaching the end opposite the corrosion coupons to a flange or fitting as required by each individual location either by welding or securing it through a drilled hole by 0.5" nuts. The initial installation of the  $\text{CaCl}_2$ -period coupons included only the hand-made coupons. A separate trip was made to Wygen 1 after receiving the standardized coupons from MSI and fabricating the 0.50"-to-0.25" adapters. The hand-made coupons were removed briefly from exposure to allow the addition of the MSI coupons to the rack assembly. This accounted for the only disturbance of these coupons during the  $\text{CaCl}_2$ -injection period. Complete coupon racks were installed for the period without  $\text{CaCl}_2$  injection, which saw or have seen no disturbances during their exposure.

During the first phase of surveillance, the hand-made coupon racks were installed on January 11, 2007 in the APH-OUT, SDA Roof, SDA-OUT and RAST while the plant was online without  $\text{CaCl}_2$  injection. Due to unsafe weather at that time, the Stack corrosion coupon rack could not be safely installed. It was later installed on January 26, 2007 by BHP personnel. The standardized (MSI) coupons were added on February 9, 2007 and each of the coupon racks was entirely removed during a planned outage on April 21, 2007 after seventy-one days of exposure. However, due to construction schedules for Wygen 2, the  $\text{CaCl}_2$  skid was removed from service on March 20, 2007. This supplied the corrosion coupons with forty days of exposure to  $\text{CaCl}_2$  injection conditions during the seventy-one day exposure period. The MSI corrosion coupons were carefully removed from the rack, placed back in their original shipping envelopes and immediately sent back to MSI for weight and corrosion loss analysis. The rough cut coupons were also carefully removed from the rack and archived for later study by project investigators.

New assemblies of corrosion coupons identical to those previously removed were installed in each of the same locations on April 22, 2007 to give comparative corrosion data after  $\text{CaCl}_2$  injection was stopped. Two sets of coupons were removed after eighty-nine days of exposure on July 21, 2007 to provide data from a similar exposure period to the first sets removed during the April 2007 outage. These two sets from the second phase of corrosion surveillance represented the two locations that saw the greatest and least amount of corrosion

from the previous phase – the SDA Roof and Stack, respectively. Coupon rack assemblies identical to the previous ones were installed in their place. They, along with the three corrosion coupon racks that were not disturbed, remain in place for extended exposure.

### **Sample Collections**

Samples of baghouse fly ash were collected by BHP personnel and subjected to lab analyses to determine what effect, if any,  $\text{CaCl}_2$  had on the physical and chemical properties of the fly ash. Samples of each were sent to Wyoming Analytical Labs for testing. The first sample was taken prior to  $\text{CaCl}_2$  injection on January 11, 2007 while the second was taken on February 9, 2007 approximately nineteen days after  $\text{CaCl}_2$  injection began at a rate of 500ppm.

### **Multi-pollutant Control Study**

Data on plant conditions was collected from the Wygen 1 Data Collection System (DCS) for the B&W study period in 2006 (2/15 – 2/22; 2/26 – 3/5; 5/15 – 5/22/06) and from Jan 1 – Aug. 16, 2007. The 2007 data incorporates both the  $\text{CaCl}_2$  injection period and period without  $\text{CaCl}_2$  injection. The task was to identify if  $\text{CaCl}_2$  injection yielded any co-benefits to other air pollution control.

B&W data (2006) showed a strong correlation between  $\text{CaCl}_2$  injection and lower mercury emissions from the stack. The data collected in 2006 and 2007 showed possible effects in the  $\text{SO}_2$  and  $\text{NO}_x$ . Because a feedback loop controls the  $\text{SO}_2$  and  $\text{NO}_x$  emissions, the usage rate of reagent used to remove them was analyzed. These results will be discussed later in this report.

## **RESULTS**

### **Corrosion Study Results**

#### **Calcium Chloride Injection Period**

The coupon racks' removal and their subsequent disassemblies were accomplished without any unintended damage to the corrosion coupons. The standardized corrosion coupons results from MSI showed the greatest corrosion loss in the regions of the SDA Roof and SDA OUT – averaging 6.17 and 5.13 mils per year (mpy) respectively. The terminal coupon on the SDA Roof assembly showed a loss rate of over 1 mpy greater than the other two standard coupons on the same assembly, while the three SDA OUT coupons' loss rates were fairly even between the three coupons in that set (see Figure 2). The other three coupon assembly locations showed less than 1 mpy average losses.

**Figure 2. BHP Wygen 1 Corrosion Coupon Results From CaCl<sub>2</sub> Addition Period**

Exposure Period: 2/9/07 - 4/21/07

Location	Coupon #	Weight Loss (g)	Mils/Year
SDA Roof	5831	0.4179	5.8578
	5832	0.4052	5.6797
	5833	0.4977	6.9763
SDA Out	5834	0.3629	5.0868
	5835	0.3700	5.1863
	5836	0.3643	5.1064
RAST	5837	0.0453	0.6350
	5838	0.0687	0.9630
	5839	0.0451	0.6322

Location	Coupon #	Weight Loss (g)	Mils/Year
APH Out	5840	0.0251	0.3518
	5841	0.0183	0.2565
	5842	0.0147	0.2061
Stack	5843	0.0158	0.2215
	5844	0.0144	0.2018
	5845	0.0147	0.2061

Table 1: Corrosion Loss Data supplied by Metal Samples, Inc.

SDA = Spray Dryer Absorber

APH = Air Preheater

RAST = Recycle Ash Slurry Tank

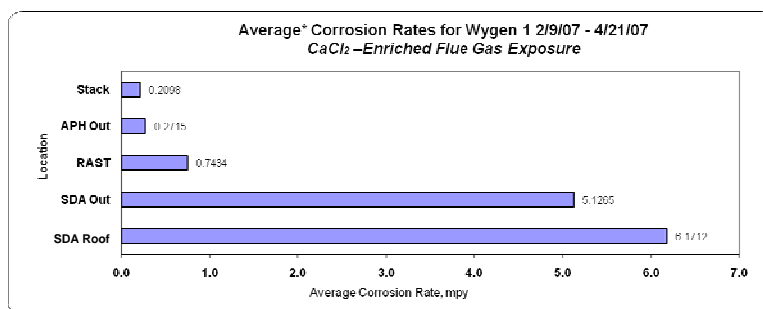


Fig. 1: Corrosion Rates from CaCl<sub>2</sub> period of Wygen 1 corrosion study, 2/9/07 - 4/21/07

\* Corrosion rates averaged from three coupons in each location

**Figure 2. BHP Wygen 1 Corrosion Coupon Results From CaCl<sub>2</sub> Addition Period**

The corrosion patterns were typically uniform on the faces of the coupons with no discernable features of note on the APH OUT, RAST and Stack locations. The general corrosion was great enough, however, on the SDA Roof and SDA OUT locations to leave discernable features on the coupons' faces.

The SDA Roof coupons' material accumulation over their surfaces was thin and generally even with no directional patterns evident. The material coating appeared to be lifted from the metal face of the coupon. (see Picture 1). After they were cleaned, raised edges could be seen in the center of the coupons on both sides where the 0.625" Teflon spacer covered the metal surface, thus protecting it from corrosion (see Pictures 2&3). There were no other notable features present on these coupons.



**Picture 1:** SDA Roof coupons after removal from CaCl<sub>2</sub>-enriched Flue Gas Exposure



**Picture 2:** Cleaned coupon from SDA-OUT after exposure to CaCl<sub>2</sub>-enriched flue gas. Notice the bullet-shaped pattern across the face. "Bullet" points downstream of flow. Dark spot is a stain on the metal surface – cause yet unknown.



**Picture 3:** Cleaned coupon from SDA Roof after exposure to CaCl<sub>2</sub>-enriched flue gas. Notice the raised area around the center chamfer caused by exposure protection from the 0.25" Teflon spacer.

The SDA OUT coupons had a similar coating of material on their surfaces as the SDA Roof specimens, but had accumulated a directionally oriented, bullet-shaped build-up of fly ash across the faces and spanning between each coupon. This build-up effectively shielded the area of the coupons covered by it from the corrosive effects of the flue gas and left distinct corrosion patterns noticeable after cleaning by MSI (see Picture 2). There were no other notable features present on these coupons.

The remaining three locations' coupons had thin, non-directional deposits on them. They yielded no discernable corrosion features after cleaning.

### **Non-injection Period**

The two corrosion coupon racks that were removed after exposure to flue gas without CaCl<sub>2</sub> enrichment were removed and disassembled without any unintended damage to the corrosion coupons. As previously mentioned, they represented the least (Stack) and greatest (SDA Roof) corrosion rate locations observed in the CaCl<sub>2</sub> injection period. Neither location showed any remarkable material loss, while both sites' coupons had fairly even weight loss throughout their respective groups. The Stack location had approximately the same corrosion rate as the previous exposure period with CaCl<sub>2</sub> injection (0.1961mpy – see Figure 3). Although the coupons sustained no unintended damage during removal from the stack port, the 0.25" nuts at each end of the three-coupon cluster had loosened by approximately two or three turns. This allowed the coupons to possibly rotate freely around the all-thread shaft, causing some weight loss by abrasion against the all-thread. This, however, has not been confirmed or quantified due to the relatively insignificant amount of weight loss difference between each exposure period.

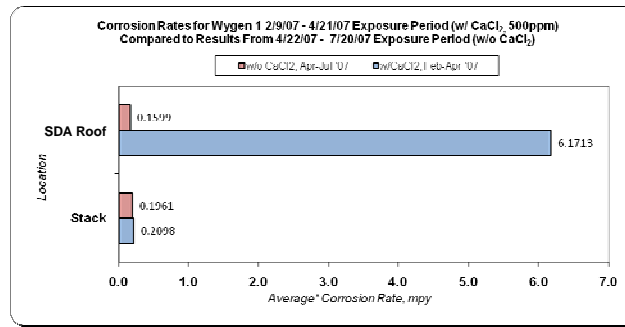
**Figure 3.** Comparison of Phases 1&2 Corrosion Results From BHP's WYGEN 1  
CaCl<sub>2</sub> Hg-Control Technology Study

Phase 1 Exposure Period, 2/9/07 - 4/21/07				Phase 2 Exposure Period, 4/22/07 - 7/20/07			
Coupon #	Location	Weight Loss (g)	Mils/Year	Coupon #	Location	Weight Loss (g)	Mils/Year
5831	SDA Roof	0.4179	5.8578	6209	SDA Roof	0.0132	0.1462
5832		0.4052	5.6797	6210		0.0165	0.1828
5833		0.4977	6.9763	6212		0.0136	0.1507
5843	Stack	0.0158	0.2215	6203	Stack	0.0157	0.1739
5844		0.0144	0.2018	6204		0.0194	0.2149
5845		0.0147	0.2061	6205		0.0180	0.1994

\*Period with CaCl<sub>2</sub> injection

\*Period without CaCl<sub>2</sub> injection

Corrosion Loss Data supplied by Metal Samples, Inc.,



\* Corrosion rates averaged from three coupons at each location

**Figure 3 Comparison of Phases 1 & 2 Corrosion Results from BHP's WYGEN 1**

The SDA Roof coupons showed a drastic decrease in corrosion loss during this exposure period, yielding a 0.1599mpy loss (see Figure 3). There were no discernable corrosion scars left on the coupons this time.

The in-house made coupons were also removed during each exposure period. They were cataloged and placed in Zip-Loc bags to be stored for later cleaning and analysis.

The Stack and SDA Roof corrosion coupon racks that were removed were again replaced with identical corrosion coupon assemblies. They, along with the remaining three corrosion coupon racks, were left in place, undisturbed, undergoing an extended exposure period. They will be removed and analyzed at a later date beyond the time of this report.

### Fly Ash Sample Analysis

The two fly ash samples that were collected were analyzed by Wyoming Analytical Labs, Inc. to determine compositional differences between each sample. The complete list of analysis results can be found in Table 1. There were no remarkable differences between the two samples for most of the analyzed parameters. The notable differences were in the Total Mercury, Chloride Leaching, Chloride Weight Percent and two other analyses involving sodium content.

**Table 1 Fly Ash Composition Analyses. Analyses performed by Wyoming Analytical Laboratories, Inc.**

Test Performed	Sample from CaCl <sub>2</sub> Injection Period	Sample from Non-injection Period	Method
% Loss on Ignition @950 C	5.02	6.30	C311(950C)
Total Arsenic, mg/kg	< 0.01	< 0.01	3052/6010
Total Mercury, mg/kg	1.2	0.64	3052/6010
Total Selenium, gm/kg	< 0.01	< 0.01	3052/6010
% Total Sulfur	4.43	4.85	3052/6010
Chloride Leaching, mg/L	1110	44	SM 4500-B
Chloride Weight %	0.444	0.025	Not Given
Silicon Dioxide, % as SiO <sub>2</sub>	26.43	28.21	Wt % Ignited Basis
Aluminum Oxide, % as Al <sub>2</sub> O <sub>3</sub>	14.53	14.82	Wt % Ignited Basis
Iron Oxide, % as Fe <sub>2</sub> O <sub>3</sub>	4.44	4.55	Wt % Ignited Basis
Calcium Oxide, % as CaO	32.72	34.15	Wt % Ignited Basis
Magnesium Oxide, % as MgO	3.96	4.13	Wt % Ignited Basis
Sodium Oxide, % as Na <sub>2</sub> O	1.59	0.71	Wt % Ignited Basis
Potassium Oxide, % as K <sub>2</sub> O	0.34	0.32	Wt % Ignited Basis
Titanium Oxide, % as TiO <sub>2</sub>	0.95	1.04	Wt % Ignited Basis
Manganese Oxide, % as MnO <sub>2</sub>	0.03	0.03	Wt % Ignited Basis
Phosphorus Pentoxide, % as P <sub>2</sub> O <sub>5</sub>	0.76	0.70	Wt % Ignited Basis
Strontium Oxide, % as SrO	0.38	0.38	Wt % Ignited Basis
Barium Oxide, % as BaO	0.50	0.49	Wt % Ignited Basis
Sulfur Trioxide, % as SO <sub>3</sub>	13.37	10.47	Wt % Ignited Basis
Alkalis as Na <sub>2</sub> O	1.81	0.92	Empirical Formula
Base to Acid Ratio	1.03	1.00	Empirical Formula
Silica Ratio	0.39	0.4	Empirical Formula
T250, Deg F	2381	2391	Empirical Formula

The CaCl<sub>2</sub>-enriched fly ash showed approximately twice the Total Mercury (1.2 mg/kg) as did the non-injection period fly ash (0.64 mg/kg). This was expected based on the earlier report from Babcock & Wilcox's mercury reduction study using the calcium chloride injection method. Their study found that injecting CaCl<sub>2</sub> onto the pre-pulverized coal effectively reduced mercury emissions in the stack. (Babcock & Wilcox, 2006). This analysis further supported that finding, indicating that the mercury is incorporated onto the solid material in the flue gas and removed primarily by the baghouses.

The Chloride Weight Percent test showed chloride content in the fly ash increased almost eighteen times in the CaCl<sub>2</sub> enriched sample after nineteen days of CaCl<sub>2</sub> injection. It increased from 0.025% to 0.444% by weight. The Chloride Leaching test was used to determine the amount of chloride, if any, readily re-dissolved back into an aqueous solution, such as in the

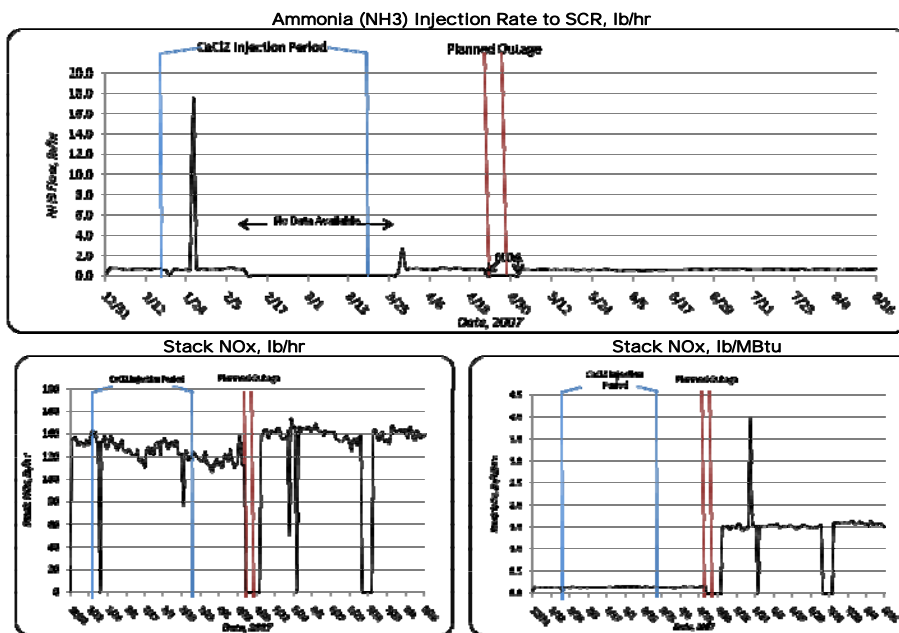
recycle ash slurry tank. The non-injection period sample yielded only 44 mg Cl/L while the  $\text{CaCl}_2$ -enriched sample yielded 1110 mg Cl/L, over a twenty-five-fold increase (Table 1).

Sodium oxide more than doubled in the  $\text{CaCl}_2$ -enriched fly ash sample as did the result for Alkalis as  $\text{Na}_2\text{O}$  (sodium oxide). The latter is a calculated value that incorporates the sodium oxide result, thus it increased by nearly the same magnitude as sodium oxide value between the two samples. The cause for this is unknown. One possible source for the additional sodium in the  $\text{CaCl}_2$ -enriched fly ash is the water used to generate the reagents such as the  $\text{CaCl}_2$  solution or the lime/recycle ash slurries. It may be the result of the treatment which the water received before being mixed with the chemical/fly ash.

### Multi-pollutant Control Results

The data collected in 2007 for stack  $\text{NO}_x$  emissions were inconclusive. Data plots for  $\text{NO}_x$  emissions measured in two different units of rate did not appear to be consistent with each other. Stack  $\text{NO}_x$  emissions reported in lb/MBtu were steadily lower before a planned April 2007 outage and suddenly increased to a much higher steady level after the outage. The  $\text{NO}_x$  emissions in pounds per hour also increased after the outage, but not to the same magnitude (see Figure 5). The  $\text{NO}_x$ -controlling chemical (ammonia) showed essentially no injection during either period, despite a large portion of the data was missing for the  $\text{CaCl}_2$  injection period (See Figure 4). No conclusive data or reports have been provided to account for this discrepancy.

**Figure 4: Black Hills Power (Wygen 1)  $\text{NO}_x$  Stack Emissions Graphs :**  
Comparing Ammonia Injection to Stack  $\text{NO}_x$  Emissions in Pounds per Hour (lb/hr) & Pounds per Million Btus (lb/MBtu)

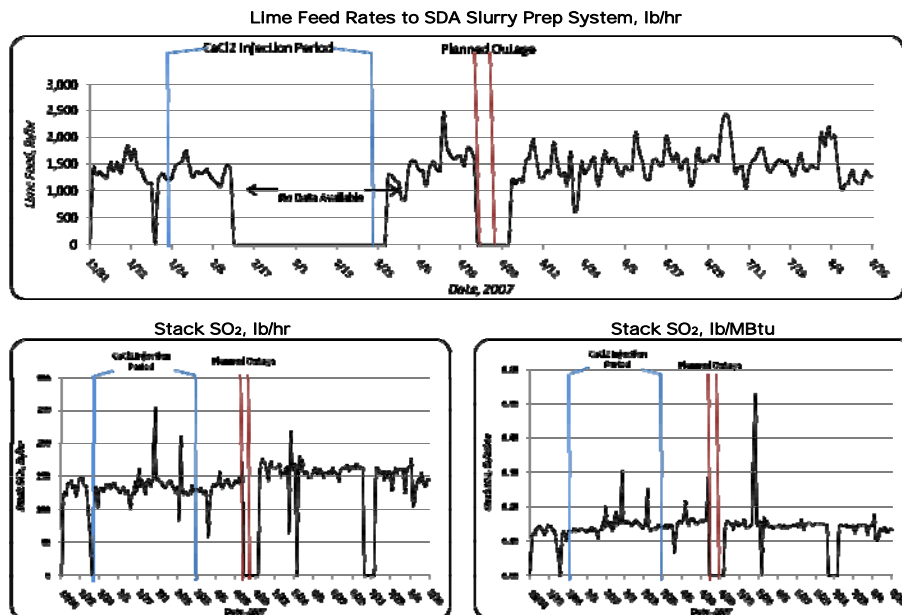


**Figure 4. Black Hills Power (Wygen 1)  $\text{NO}_x$  Stack Emissions Graphs**



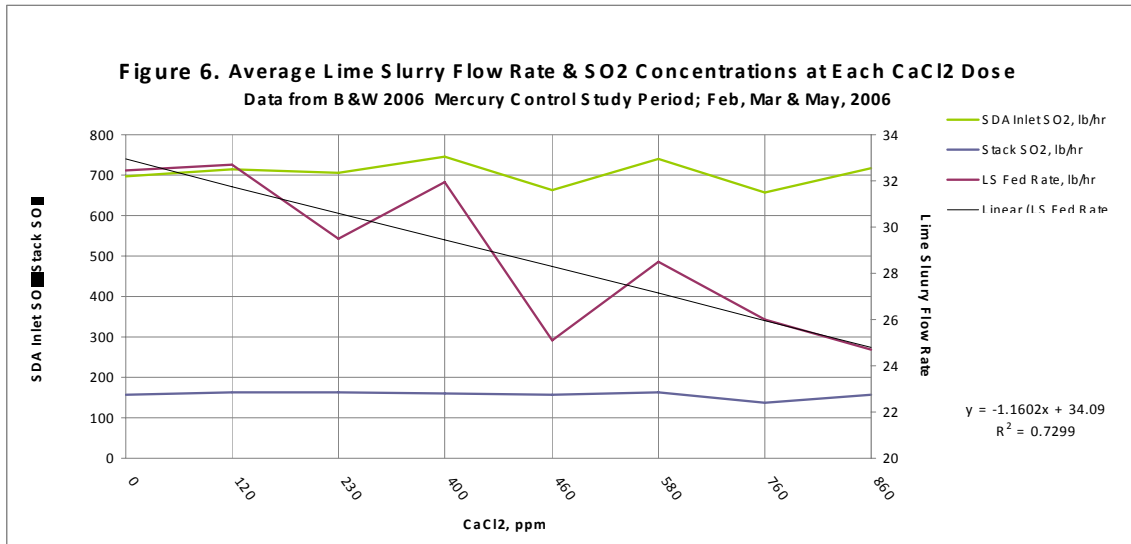
The 2007 SO<sub>2</sub> emissions at the stack showed little difference in the averages between the two condition periods (see Figure 5). While there was slightly more lime fed on average during the period without CaCl<sub>2</sub> injection, it mirrored the trend in SO<sub>2</sub> (lb/hr) at the stack, which was also higher by approximately the same magnitude. Average sulfur emissions on a lb/MBtu basis were kept the same between the injection and non-injection periods (0.15 lb SO<sub>2</sub>/MBtu per period). As with the ammonia injection data, a large portion of lime feed data was missing during the CaCl<sub>2</sub> injection period, which lowers confidence in the results from that period.

**Figure 5: Black Hills Power (Wygen 1) SO<sub>2</sub> Stack Emissions Graphs :**  
Comparing Lime Feed Rates to Stack Emissions in Pounds per Hour (lb/hr) & Pounds per Million Btus (lb/MBtu)



**Figure 5. Black Hills Power (Wygen 1) SO<sub>2</sub> Stack Emissions Graph**

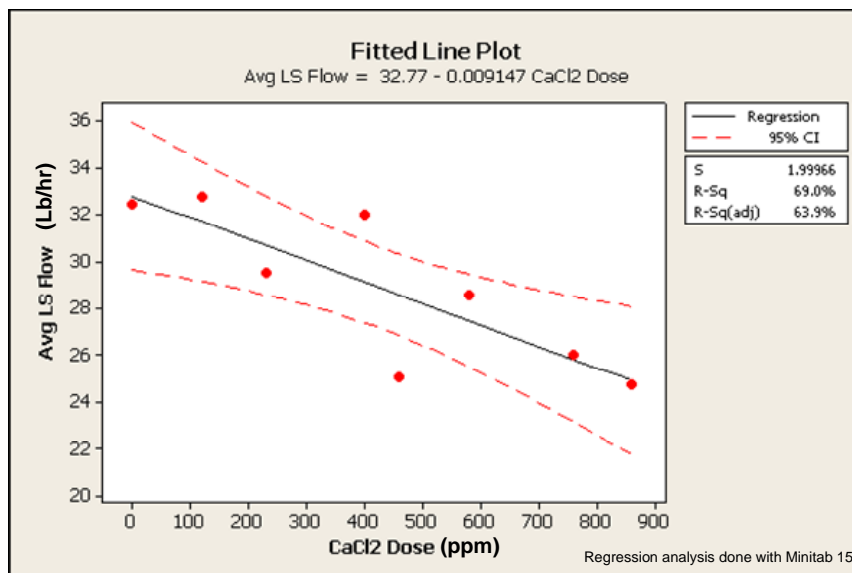
Data were available from the 2006 B&W mercury test period that allowed for an analysis of the effects of CaCl<sub>2</sub> on SO<sub>2</sub> emissions. The data show a fairly strong correlation between CaCl<sub>2</sub> dose and lime slurry usage. SDA inlet SO<sub>2</sub> concentrations averaged a steady trend around 712 lb/hr and the stack saw a steady average of 157 lb/hr (see Figure 6).



**Figure 6. Average Lime Slurry Flow Rate and SO<sub>2</sub> Concentrations at Each CaCl<sub>2</sub> Dose**

Over this same time period, lime slurry usage tended to decrease as CaCl<sub>2</sub> doses increased. A statistical analysis of the average lime slurry usage during each level of CaCl<sub>2</sub> dosage was performed. The student's t-distribution was used and yielded an  $\alpha$  of 0.005. Also, regression analysis gave an  $R^2$  value of 0.7299 (Figure 6&7). This shows that it is highly probable that, given the way in which the data were collected, the CaCl<sub>2</sub> had a beneficial effect on SO<sub>2</sub> reduction. Insufficient data did not allow the same analysis to be performed on NO<sub>x</sub> emissions for the 2006 B&W study.

**Figure 7. Lime Slurry Regression Analysis During Various  $\text{CaCl}_2$  Doses from 2006 Babcock & Wilcox Mercury Control Study**



**Figure 7. Lime Slurry Regression Analysis During Various  $\text{CaCl}_2$  Doses from 2006 Babcock and Wilcox Mercury Control Study**

## DISCUSSION

### Corrosion Study

The data show that the corrosion effects during the  $\text{CaCl}_2$  injection period centered mainly around the SDA vessel. The primary suspected cause for this is the introduction of elevated chloride levels from the recycle ash slurry portion of the slurry fed to the SDA atomizer head tank. The SDA Roof coupons averaged 6.1713 mpy under  $\text{CaCl}_2$  injection conditions and 0.1599 mpy when no  $\text{CaCl}_2$  was being injected. This caused us to investigate the abundance of chloride in the two ash samples that were collected. As stated earlier in this report, the concentration that leached back into aqueous solution was over twenty-five times higher during the  $\text{CaCl}_2$  injection period according to laboratory results (see Table 1). It is hypothesized that the vigorous agitation in the lab tests resembles the conditions found in the recycle ash slurry tank, which receives recycled ash from the baghouse hoppers. The initial chloride contained on this ash is believed to leach back into solution during the vigorous mixing in this tank and then re-introduced to the flue gas stream via the SDA atomizer. This recycled chloride is believed to be added to the concentration of chloride in the incoming flue gas and thus leads to a higher chloride concentration in the SDA vessel and SDA outlet regions. As this recycling of chloride-enriched ash continues, more chloride enrichment of the ash and thus recycle ash slurry occurs, leading to higher chloride concentrations in the SDA regions and the inlet chambers of the baghouse before fly ash is filtered out by the fabric filters (“bags”). The chlorides are believed to

stay with the fly ash and not the flue gas as the coupons in the stack showed negligible corrosion (~0.2 mpy) during both injection and non-injection periods (see Figure 3).

Despite the likelihood of high chloride concentrations in the recycle ash slurry during periods of  $\text{CaCl}_2$  injection, the coupons removed from the RAST showed an average of only 0.7434 mpy (see Figure 2). Because of the vigorous turbulence and velocity in this environment, it is unclear just how much material loss was due to erosive effects from the entrained fly ash as opposed to actual corrosion caused by immersion in the slurry. Although the high velocities and turbulence may cause erosive losses, they may actually help protect against corrosion, especially pitting attack, despite the likelihood of elevated chloride levels (Fontana, 1986). In either case, the coupons appeared to be protected, at least in part, by a heavy layer of fly ash deposits that encased each coupon. This heavy layer of material was also noticed on the walls of the recycle ash slurry tanks as they were being drained during a planned outage, which may offer the same protection against corrosion.

As mentioned earlier in this report, the 0.625" spacers protected the centers of the coupons from corrosion. A spacer of this diameter was needed due to the 0.5" chamfered center hole. It helped ensure consistent spacing between each coupon. The coupons were selected without realizing that the center hole was chamfered. Since this portion of the surface area was not exposed and the corrosion calculation does not take this into account, the reported corrosion rates are lower than the true corrosion rates. Future corrosion experiments should minimize this covered area and expose as much surface area as possible. Despite this oversight in coupon rack design, the corrosion surveillance still yields valid information as to what areas of the flue system will be prone to elevated corrosion rates during periods of  $\text{CaCl}_2$  injection.

The rough cut corrosion coupons fabricated by BHP personnel have not yet been cleaned. These coupons are intended to be a qualitative study of the corrosion surveillance. It is recommended by MSI that the standardized corrosion coupons be sent back to them without delay upon removal, thus leaving too little time to observe their corrosion deposits under magnification in the lab. The rough cut coupons supplied by BHP were only weighed to the nearest 0.1 gram, making a weight loss analysis unreliable. Other problems with relying on these coupons for accurate corrosion loss data include the inconsistency of the coupon surface area covered by each rubber washer placed between the coupon and the 0.5" nut, the variable surface areas of the coupons due to cutting inaccuracies and the possible contamination of the stock metal from which they were cut while being stored in the metal shop. Also, the high localized heat caused by the cutting torch may have changed the metallurgical properties along the outer edges. Thus, these specimens can be archived for extended periods for later observations.

### **Multi-pollutant Control Study**

The fact that the 2007  $\text{NO}_x$  data does not mirror simultaneous trends in two different units of rate measurement is unexpected, as well as unexplained. One would expect to see similar

trend patterns and magnitudes of change for the same NO<sub>x</sub> emissions between different emission rate units. The only sufficient data for analysis were regarding SO<sub>2</sub> emissions. Lime slurry is the SO<sub>2</sub> controlling reagent and a cost to the power plant. Sufficient lime slurry will be used to maintain the stack SO<sub>2</sub> emissions just under permit limits, according to operational practices. Thus, as the data show, the stack SO<sub>2</sub> emission rate will remain fairly constant. Lime slurry demand becomes the indicator as to how the CaCl<sub>2</sub> performs with the SO<sub>2</sub> emissions. As the data show, lime usage during the 2006 B&W CaCl<sub>2</sub> tended to decrease with increasing CaCl<sub>2</sub> doses (see Figure 6), while it made no significant changes in 2007 (Figure 7).

The 2006 B&W study data that showed a response in decreased lime usage with increased CaCl<sub>2</sub> doses were not collected during a test designed to test the effects of CaCl<sub>2</sub> on SO<sub>2</sub>, but rather on mercury. To better study this effect and to gain better statistical confidence, the test should be conducted with CaCl<sub>2</sub> doses chosen at random. Also, the amount of data (counted in hours) varied greatly between the CaCl<sub>2</sub> doses. Some CaCl<sub>2</sub> dose periods had a mere 10 hours of data to average, while others had as much as 261 hours. Since it is not well understood how long the change in CaCl<sub>2</sub> dose takes to affect the lime slurry demand, a longer run time at each dose would help generate better confidence in the averages and conclusions. Similarly, the 2007 CaCl<sub>2</sub> injection period was enacted to provide data on corrosion instead of effects on SO<sub>2</sub> emissions. This was not a test plan designed to test SO<sub>2</sub> responses to CaCl<sub>2</sub> injection. Furthermore, in neither case was the power plant run as a controlled test facility. Numerous variables may have played a role in the CaCl<sub>2</sub>/SO<sub>2</sub> interaction, and should therefore be kept in mind when assessing these results.

## **Sample Collection**

A single fly ash sample was taken of the CaCl<sub>2</sub> injection period and therefore should not be construed as a maximum value during a more extensive injection period. The sample of CaCl<sub>2</sub>-enriched fly ash indicates that the chloride levels in the ash do increase during CaCl<sub>2</sub> injection, but no data exist to show what a maximum fly ash chloride-saturation value is or the rate with respect to time at which that theoretical maximum is achieved during a steady CaCl<sub>2</sub> injection. It should not be asserted that the chloride values reported for this fly ash sample directly yield the amount of corrosion seen during this surveillance period.

The chloride values reported for the fly ash sample collected during a non-injection period can be assumed to be the maximum values. The sample was collected on January 11, 2007 and the last reported date of CaCl<sub>2</sub> injection prior to that was on October 26, 2006. This should be ample time to reach steady-state conditions regarding chloride levels associated with the fly ash.

## **CONTINUING RESEARCH**

### **Corrosion Surveillance**

Coupon racks are still in place at Wygen 1 undergoing extended exposure to non-injection conditions. Corrosion racks in the APH-OUT, SDA-OUT and RAST locations have been undisturbed since being installed on April 22, 2007. The corrosion racks currently in place at the SDA Roof and Stack locations were installed on July 21, 2007, immediately after removing the two locations' racks as discussed earlier in this report. These racks will be removed at a later date to assess corrosion losses.

### **Fly Ash Corrosivity Experiments**

Laboratory experiments are underway at the University of Wyoming's College of Engineering and Applied Science (UW-CEAS) to test the corrosivity of the fly ash under both room and elevated (60°C) temperatures and moisture levels. Corrosion coupons are being exposed to "dry" fly ash from both the injection and non-injection periods at elevated and room temperatures to help determine if the fly ash itself is corrosive without the added effects of velocity, erosion and moisture, such as in the hopper sections of the baghouse and associated conveyors and chutes where the fly ash from the fabric filters collects to be either disposed of or used in the recycle ash slurry system.

A similar experiment is being conducted to determine the corrosivity of the fly ash when it is in aqueous slurry. Corrosion coupons are being exposed to stagnant mixtures of distilled water and fly ash from each 2007 injection condition in glass tubes to help determine the corrosivity of the slurry without the erosive velocity effects and possibly without the potential protection of layers of material that are present and have been observed in the recycle ash slurry tank and its related coupons. A set of these experiments is being done at both room and elevated (60°C) temperatures.

### **Additional Future Experiments and Research**

Other academic studies will be implemented in the future to gain further knowledge and insight of this and related research. Facilities at UW-CEAS are able to support a wide variety of experiments that are in the conceptual or design phases. The two samples of fly ash and others collected in the future will be looked at under a scanning electron microscope to determine if any differences exist in the physical characteristics of the fly ashes. Laboratory studies of flue gas corrosivity at operational temperatures and pressures are being planned. Corrosion studies similar to those described in 5-b, but under varying doses of  $\text{CaCl}_2$  are a possibility also. Field studies to assess the long-term effects of  $\text{CaCl}_2$  injection have been discussed for BHP's new Wygen II power plant. These and other experiments will be carried out by current and future academic researchers.