

THE ROLE OF CALCIUM IN FOULING OF WESTERN COALS

B. Ziesmer
Northern Indiana Public Service Company
Combustion Applications Department
5265 Hohman Avenue
Hammond, IN 46320

and

R. Hatt
Island Creek Corporation
2365 Harrodsburg Road
Lexington, KY 12029



Rod Hatt

rod_hatt@coalcombustion.com

114 S Main St
Versailles, KY 40383

Office 859-873-0188

ABSTRACT

This paper discusses the effect that calcium in western coals has on fouling of convection passes of pulverized coal (PC) and cyclone-fired utility boilers. Significant problems with fouling of the convection passes in four PC fired boilers and one cyclone-fired boiler were encountered when burning a high volatile bituminous Wyoming coal. This lignitic ash coal would typically be classified low fouling because sodium in the ash was less than 1%. Field experience showed a direct correlation between calcium content and fouling. Major and minor elemental analyses of the deposits showed high calcium and sulfur. Polarized light microscopy (PLM) and SEM/EDAX analyses of the deposits showed that the principal bonding agent was a calcium and sulfur-rich material, probably calcium sulfate.

THE ROLE OF CALCIUM IN FOULING OF WESTERN COALS

It is common knowledge that the fouling of boiler convection passes is at least partially dependent on the chemical constituents of fly ash. Traditionally, it is thought that the fouling of eastern coals is dependant on the base-to-acid ratio and the sodium content of the ash.¹ It has been thought that fouling of western coals' fly ash was predominantly determined by the sodium content.² A recent paper indicates that high calcium³ content can exacerbate the sodium induced fouling tendency of western coals.³ Experience by NIPSCO has demonstrated calcium cannot only exacerbate sodium induced fouling but can also be the primary cause of fouling.

NIPSCO first experienced fouling problems in the horizontal convection passes of four pulverized coal (PC) and one large cyclone-fired boiler in 1982. The fouling was experienced in a section where flue gas temperatures are 1300-1500°F (720-840°C). The fouling was characterized by hard deposits found in the back spaces. In the case of the PC units, fouling progressed into the side spaces until excessive gas side pressure drop limited load and forced the units off line for cleaning (high pressure water blasting was found to be the most successful technique). The PC units had to be taken off line every six weeks

when the fouling problem was most severe. In the case of the cyclone-fired unit, fouling never progressed to the point where there was extensive fouling of the side spaces but fouling of the back spaces did decrease heat transfer significantly.

This problem was puzzling for several reasons:

1. The coal had been burned (eight months in the PC units and intermittently for three years in the cyclone unit) without encountering significant fouling problems.
2. Unit operating parameters were essentially unchanged except the PC units were running less at high load and more at low load.
3. The sodium content of the coal was low (0.5-1.0%).
4. Proximate coal quality characteristics were unchanged (11,000 Btu/lb, 5% ash, 12% moisture, 0.6% sulfur).
5. Excessive ash or flue gas moisture was not contributing to the fouling problem due to the high proximate quality of the coal.

Even more troubling was comparing the cyclone-fired unit, designated by NIPSCO as Unit 14, to a duplicate boiler, Unit 12, which burned high sulfur Illinois #5 and #6 seam coal. Typically the high sulfur coal burned in Unit 12 would be classified medium fouling coal. Unit 12 had a higher capacity factor due to the lower price of local high sulfur coal compared to Unit 14's low sulfur coal. Unit 12's sootblowing was less frequent than Unit 14's sootblowing. Yet Unit 14 experienced a fouling problem while Unit 12 never had more than a light coating of ash in the horizontal convection pass.

An extensive deposit sampling and analysis program was initiated to determine the cause for the deposit problem.

DESCRIPTION OF UNITS

NIPSCO's D. H. Mitchell Generating Station has four units designated units 4, 5, 6, and 11 (NIPSCO has a rather unique system of numbering the units sequentially for the history of the company as opposed to on a station basis). All these units are pulverized coal fired, dry bottom boilers. Units 4, 5 and 6 are essentially duplicate Combustion Engineering tangentially fired twin furnace boilers. These units have a design main steam flow of 860,000 lbs./hr. and a reheat flow of 757,000 lb./hr. and steam conditions of 1850/1005/1005. These units are currently rated by NIPSCO at 133 MWg. These boilers had in service dates of 1956, 1958, and 1959, respectively. Each boiler is serviced by four CE RB673 mills. Each mill services one elevation of coal nozzles. Since this is a twin furnace design, there are eight coal nozzles (four for each furnace) supplied by each pulverizer. These pulverizers have a base capacity of 41,500 lb/hr. for 55 grind coal assuming 70% of the pulverized coal passes through a 200 mesh screen.

These boilers are controlled circulation, drum type boilers which utilize burner tilt and excess air for steam temperature control. They were originally designed to burn Illinois basin #6 seam coal such as River King. Accordingly, they were designed to handle a fairly high slagging, low fouling coal. The furnace liberation is fairly generous, 81,500 Btu/sq. ft./hr. The heat input per plan area is 1.71 MBtu/hr-sq. ft. Unfortunately, the convection pass was not as conservatively designed. The horizontal primary superheater has clear side spacing

of only 1 1/32" and the economizer has side spacing of only 1 1/8". In addition the economizer is a staggered finned tube economizer.

The remaining unit at the D. H. Mitchell Generating Station, Unit 11, is a Babcock & Wilcox front wall fired, drum type boiler (B&W contract RB-456). This boiler has a conservatively designed furnace with a heat liberation of 71,800 Btu/sq. ft.-hr. and heat input per plan of 1.36 MBtu/sq. ft.-hr. This unit was less troubled by fouling problems since it was not operated for any extensive period of time during the excursion in coal quality of the Wyoming A coal which caused fouling problems.

NIPSCO also has two essentially duplicate once-through, cyclone-fired, super-critical boilers. One of these boilers, Unit 12 (B&W contract UP-76), is located at NIPSCO's Michigan City Generating Station. This unit had an in service date of 1974 and has always burned high sulfur Illinois basin coal. The second unit, designated Unit 14 (B&W contract UP-112), is located at NIPSCO's R. M. Schahfer Generating Station. This unit had an in service date of 1976 and has always burned low sulfur compliance (1.2 lbs. SO₂/MBtu) coal. The unit was switched to low sulfur design in the middle of the construction of the unit. There were no modifications to the unit that were made to accommodate burning western coal other than the installation of a hot side precipitator.

Many early B&W once-through, cyclone-fired boilers experienced significant operating problems and B&W changed a number of design standards in the middle 1960s in response to these operating problems. Both of these cyclone-fired boilers discussed in this paper were designed to most of the new B&W standards. This means that these units incorporate a sloped floor, gas recirculation and gas tempering, dust collectors ahead of the gas recirculation fans, lower heat input per cyclone, lower heat input per plan area, lower FEGT (furnace exit gas temperature), wider convection pass spacing, tight cased roof, slag screen ahead of the air heaters and better (more numerous) wall blowers and retractable soot blowers. Additionally, both these units have a furnace nose, unlike many early B&W once-through, cyclone-fired boilers. Both these boilers were designed with a main steam flow of 3,212,000 lbs./hr and a reheat flow of 3,144,000 lbs./hr. Steam conditions are 3635 psi/1005/1005. Unit 12 has a design electrical output of 521 MW and Unit 14 was designed to be approximately the same size. These units were designed for severe slagging, high fouling coal.

All the NIPSCO units discussed in this paper use air as the sootblowing medium.

COAL

The western coals that were burned were from South Central Wyoming. The Wyoming A coal was deep mined utilizing one continuous miner and one long wall miner. Since the continuous miner and the long wall miner took a smaller cut than the seam thickness, there was little out of seam dilution with this coal.

Four typical analyses for the Wyoming A coal are shown in Table I. Each column represents Wyoming A coal at a different point in time - one for coal prior to the fouling problem, one for a typical analysis at the beginning of the fouling problem, one typical of severe fouling, and one for a typical analysis after the fouling problem was resolved. The fouling problem began when the base-to-acid ratio of the Wyoming A coal increased dramatically due to changes in the ash chemistry of coal in the center and top of the seam (where coal was being mined). The fouling problem was resolved when the base-to-acid ratio of the coal was reduced below 1.0.

The coal company was able to reduce the base-to-acid ratio by changing operation of their continuous miner. The continuous miner began to take coal from a lower part of the seam where the ash content was higher, the silica content of the ash was higher, and the calcium content was lower. The net effect of mixing this coal from the continuous miner with the coal produced by the long wall miner was the coal shown in Table I as the "after fouling" coal. You will notice that the ash content has increased about 1% and the base-to-acid ratio has reduced from 1.42 to 0.80. Since the other elements in the ash stayed approximately the same except for calcium and silica, one can see how the dramatic decrease in calcium content and increase in silica content changed the coal from a fouling to a non-fouling coal.

The ash mineral characteristics of the coals in Table I have been tabulated in Table II on a sulfur trioxide (SO_3) free basis in order to make comparisons of the ash mineral characteristics in each of these coals more relevant. It is interesting to note that Wyoming A coal in the after fouling condition had higher sodium than when this coal was causing a fouling problem, further indicating that sodium was not an important factor contributing to this fouling problem.

Wyoming B coal was strip mined coal. The coal came from a variety of seams (none of the seams were the same as Wyoming A coal). A typical analysis of this coal is shown in Table III. This coal was burned in the PC units without encountering fouling problems, but a perfect comparison to Wyoming A coal cannot be made since the Units had lower capacity factors when burning the Wyoming B coal. Nonetheless, it is felt there has been enough operating experience to classify this coal as low to medium fouling coal.

The high sulfur coal burned in one of the duplicate cyclone-fired boilers was principally from two mines located in Illinois. One mine was located in Douglas County, Illinois and provided raw Illinois #5 and #6 seam coal. The other mine, located in Perry County, Illinois, is a washed Illinois #6 seam coal. Typical analyses of both these coals is shown in Table III.

DEPOSIT SAMPLING AND ANALYSIS

Samples of deposits from the D. H. Mitchell Generating Station boilers were collected using a modification of British Standard 2455 Part 2. This procedure ensures a representative sample of the deposits. Samples of coal, furnace deposits, horizontal primary superheater deposits (pluggage) and flyash were collected. ASTM major and minor elemental analyses were performed and are shown in Table IV. The pluggage had considerably more calcium and sulfur in comparison to the coal, furnace deposit and fly ash. This was the first indication that the deposit could be held together by a fouling type agent like Calcium Sulfate ($CaSO_4$).

In fouling type deposits, the ash is not necessarily fused but held together with a bonding agent. Optical polarized light microscopy (PLM) and scanning electron microscopy (SEM) are good tools for determining the morphology and simple chemistry of ash deposits. Figure 1 is a polarized light microphotograph of the deposit taken from the horizontal primary superheater, DHMGS Unit 6. As can be seen, there are central cores of fly ash surrounded by a crystalline material. Figure 2 is the same sample shown using crossed polarized filters. The birefringence of the crystalline material bonding the fly ash shows up as light on the dark background. This optical analysis of the deposits further indicated that a fouling mechanism was taking place.

General chemistry of the fly ash and bonding material can be determined using

SEM and energy dispersive x-ray analysis. The fly ash was generally high in silica and alumina and was similar to non-fused fly ash. The material bonding the fly ash together was composed of calcium and sulfur. Figure 3 is an electron microphotographic of the deposit from the horizontal primary superheater. Although not presented here, many samples of the deposits were analyzed in this way with techniques such as dot mapping of elements and pinpoint analyses being used.

These methodologies support the hypothesis that the fouling was caused by a calcium sulfur, probably calcium sulfate, type material bonding the fly ash together.

CONCLUSIONS

NIPSCO's experience indicates that calcium can cause fouling of boiler convection passes. There is some indication that calcium-to-silica or base-to-acid ratios may be important in predicting the fouling characteristics of a high calcium coal.

Further research should be conducted to determine how these ratios affect the fouling tendency of high calcium coal. Research into the effect of organic versus inorganic calcium on fouling should also be conducted. Additional analytical work on this type of fouling could examine the chemistry of weak acid soluble materials in the ash deposits, with microscopic examination of the remaining material. Hopefully, a combination of the field experience of other users and additional research can be used to develop a quantitative method for predicting the fouling tendency of a coal taking into account both calcium and sodium.

ACKNOWLEDGMENTS

The authors would like to acknowledge the optical microscopic analysis of deposits provided by Mike Bayrd, Particle Data Laboratories. The advice and review of this work and conclusions by Robert P. Hensil, Mooresville, N.C., is also greatly appreciated.

REFERENCES

1. R. C. Attig and A. F. Duzy. "Coal Ash Deposition Studies and Application to Boiler Design." American Power Conference, April 22, 1969.
2. E. C. Winegartner. "Coal Fouling and Slagging Parameters." ASME Research Committee on Corrosion and Deposits from Combustion Gases, 1974.
3. R. W. Bryers. "Examination of Fouling of Convective Heat Transfer Surface by Calcium and Sodium Using Micro-Analytical Techniques." Joint Power Generation Conference, 86-JPGC-FACT-5, Portland, Oregon, October, 1986.

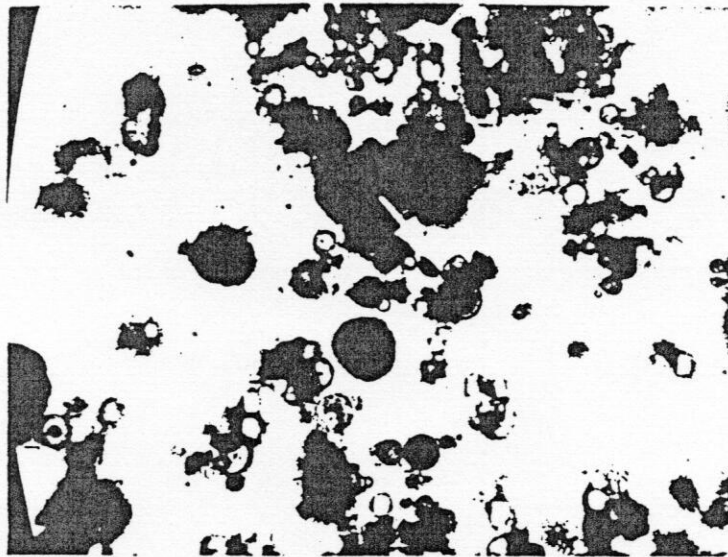


Figure 1. Optical photograph of reheater deposit from PC fired boiler under bright field at 320X magnification.

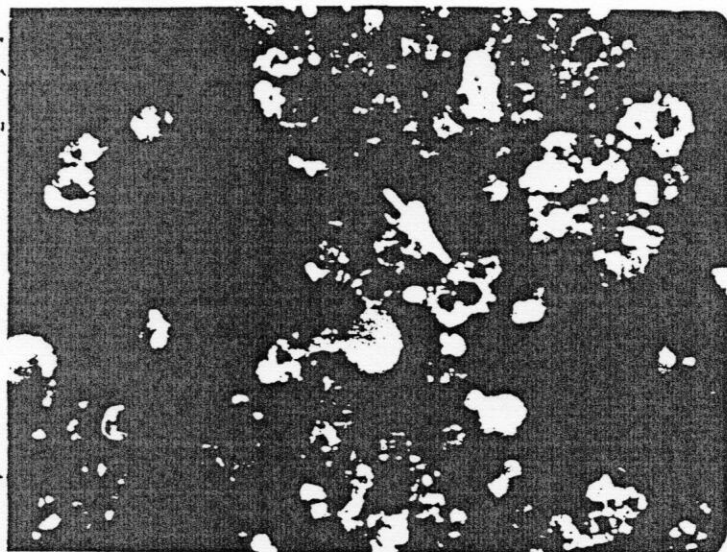


Figure 2. Optical photograph of reheater deposit from PC fired boiler under polarized light illumination at 320X magnification.

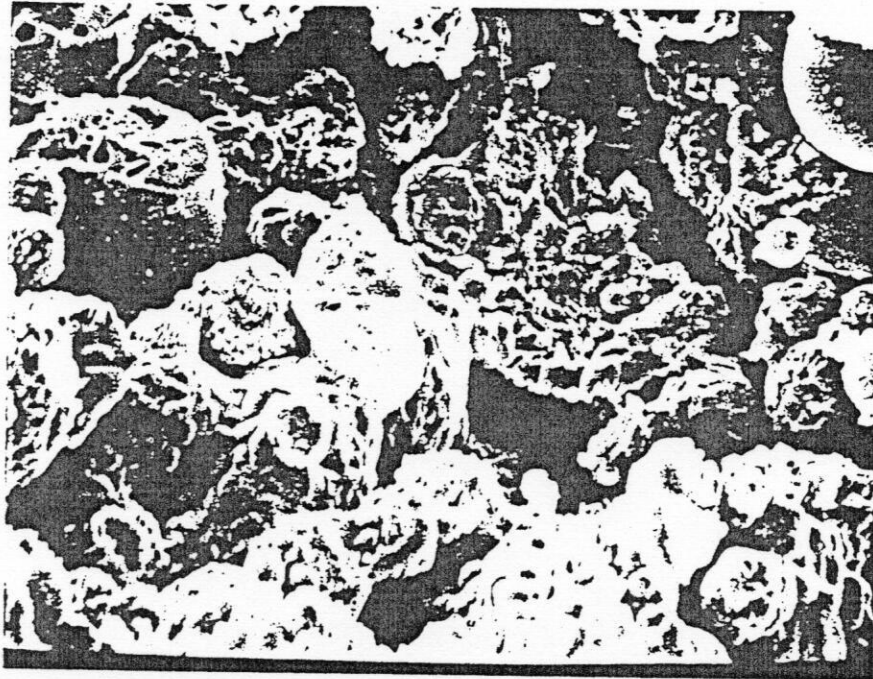


Figure 3. Scanning electron microscope image-2000X-Unit 6 (PC fired) horizontal primary superheater deposit. Fly ash is in upper right hand corner. Calcium sulfates is in lower right hand corner.

TABLE I - TYPICAL COAL ANALYSES

Wyoming Coal A

As Received Basis	<u>Before Fouling</u>	<u>Fouling</u>	<u>Severe Fouling</u>	<u>After Fouling</u>
Gross Calorific Value (Btu/lb.)	11,054	11,050	10,890	10,853
Volatile Matter (%)	37.8	37.8	37.7	37.1
Fixed Carbon (%)	43.3	44.1	44.3	42.5
Moisture (%)	12.6	13.1	14.8	12.6
Ash (%)	5.5	5.1	4.9	6.5
Sulfur (%)	0.6	0.56	0.5	0.5
Ash Fusion Temperatures (°F)				
Initial Deform (red)	2098	2313	2470	2161
Softening (red)	2208	2369	2595	2189
Hemispherical (red)	2247	2400	2640	2218
Fluid (red)	2309	2438	2700	2243
Initial Deform (oxid)	2165	2355	2525	2174
Softening (oxid)	2277	2409	2640	2211
Hemispherical (oxid)	2322	2438	2685	2252
Fluid (oxid)	2383	2474	2700	2290
Major and Minor Elements (%)				
Silica (SiO ₂)	29.42	24.20	21.60	32.23
Alumina (Al ₂ O ₃)	14.43	13.29	12.20	13.80
Titania (TiO ₂)	0.76	0.74	0.73	0.70
Iron (Fe ₂ O ₃)	8.61	8.39	8.14	7.33
Calcium (CaO)	20.06	26.20	30.92	21.52
Magnesia (MgO)	7.47	7.99	8.89	6.77
Potassium (K ₂ O)	0.78	0.53	0.38	1.02
Sodium (NaO)	0.46	0.66	0.55	0.76
Sulfur Trioxide (SO ₃)	16.90	16.29	15.25	14.55
Phosphorous Pent. (P ₂ O ₅)	0.43	0.72	0.75	0.61
Und.	0.68	0.99	0.59	0.71
Base to Acid Ratio	0.84	1.14	1.42	0.80

TABLE II

MAJOR & MINOR ELEMENTS (Sulfur Trioxide Free Basis)

Wyoming

Coal A

	<u>Before Fouling</u>	<u>Fouling</u>	<u>Severe Fouling</u>	<u>After Fouling</u>
Silica (SiO ₂)	35.40	28.91	25.49	37.72
Alumina (Al ₂ O ₃)	17.36	15.88	14.40	16.15
Titania (TiO ₂)	0.91	0.88	0.86	0.82
Iron (Fe ₂ O ₃)	10.36	10.02	9.60	8.58
Calcium (CaO)	24.14	31.30	36.48	25.18
Magnesium (M _g O)	8.99	9.54	10.49	7.92
Potassium (K ₂ O)	0.94	9.63	0.45	1.19
Sodium (NaO)	0.55	0.79	0.65	0.89
Phosphorous (P ₂ O ₅)	0.52	0.86	0.88	0.71
Undetermined	0.83	1.19	0.70	0.84

TABLE III - TYPICAL COAL ANALYSES

As Received Basis	Wyoming	Illinois	
	<u>B</u>	<u>Raw</u>	<u>Washed</u>
Gross Calorific Value (Btu/lb.)	9680	10,436	11,043
Volatile Matter (%)		30.63	36.20
Fixed Carbon (%)		42.24	41.45
Moisture (%)	17.29	15.37	12.61
Ash (%)	9.09	11.76	9.74
Sulfur (%)	0.52	2.64	2.95
Ash Fusion Temperatures (°F)			
Initial Deform (red)	2111	2040	2000
Softening (red)	2150	2130	2060
Hemispherical (red)	2181	2230	2080
Fluid (red)	2302	2325	2290
Initial Deform (oxid)		2375	2290
Softening (oxid)		2450	2390
Hemispherical (oxid)		2495	2430
Fluid (oxid)		2540	2500
Major and Minor Elements (%)			
Silica (SiO ₂)	41.45	47.38	50.78
Alumina (Al ₂ O ₃)	12.95	19.85	19.90
Titania (TiO ₂)	0.51	1.01	0.14
Iron (Fe ₂ O ₃)	6.81	22.70	16.70
Calcium (CaO)	23.43	2.10	3.34
Magnesia (MgO)	3.58	0.99	0.85
Potassium (K ₂ O)	1.57	1.95	2.17
Sodium (NaO)	0.57	1.02	1.35
Sulfur Trioxide (SO ₃)	8.18	1.07	3.68
Phosphorous Dent. (P ₂ O ₅)	0.47	0.22	0.20
Und.	0.48	1.71	0.09
Base to Acid Ratio	0.65	0.42	0.34

TABLE IV - COMPARISON OF MAJOR & MINOR ELEMENTS
DHMGS UNIT 6 PC CE BOILER

	<u>Coal A</u> <u>Fouling</u>	<u>Furnace</u> <u>Red Hard</u>	<u>Top of HPSH</u> <u>Red Hard Large</u>	<u>Fly Ash</u>
SiO ₂	24.20	23.7	15.3	31.2
Al ₂ O ₃	13.29	10.7	9.3	14.5
TiO ₂	0.74	0.5	.5	0.8
Fe ₂ O ₃	8.39	28.3	7.8	9.2
CaO	26.20	16.0	28.0	30.9
MgO	7.99	2.8	6.4	8.2
K ₂ O	0.53	0.9	0.4	.6
Na ₂ O	0.66	1.5	0.5	1.11
SO ₃	16.29	14.0	30.3	2.4
P ₂ O ₅	0.72	0.2	0.2	.5