

Role of Sodium in Coal in Determining Deposition Rates

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ABSTRACT: The alkali content in the ash is commonly thought to be the “bad actor” in determining coal ash deposition rates on boiler heat transfer surfaces. This paper reports results of 16 tests in which ash aerosol deposition rates were measured for three coals, burned under air- and oxy-fired combustion conditions. A 100 kW down-fired laboratory combustor coupled with a specially designed deposition probe was employed. Ash aerosol particle size distributions and size-segregated compositions were measured using electric-mobility, light-scattering, and low-pressure impactor techniques. Net sodium vaporization (assumed to be the fraction of sodium collected as a $<0.6\ \mu\text{m}$ fume) was compared to literature data. For ash deposition rates, emphasis was on the tightly bonded “inside” deposits rather than the loosely bound “outside” deposits, which could not be collected or weighed precisely. Over a limited range of these tests, where PM_{10} was indeed greatly enriched in sodium, deposition rates did correlate with the sodium content of PM_{10} and the ratio of $\text{Na}/(\text{Al} + \text{Si})$ in the coal, as proposed in the literature. However, over the entire range of deposition rates investigated, the measured rates did not correlate well with the sodium content of the coal or with the sodium content of the fine ash aerosol (PM_{10} or $\text{PM}_{0.6}$) but did correlate well with the overall flue gas concentration of PM_{10} , of which the alkali composition varied significantly over the 16 tests. This suggests a mechanism of deposit adhesion that depends simply upon the presence of sub-micrometer particles of any composition. Additional research to confirm this would be useful because this conclusion disagrees with most existing models for ash deposition. This work focuses on the inside fouling deposition, which could be seen as the initial layer of the fouling deposits. Slagging deposition is not within the scope of this work.

1. INTRODUCTION

Fouling of heat transfer surfaces is a serious operational problem in boilers. Alkali metals, namely, sodium and potassium, have been associated with the formation of hard-bonded deposits on the convection and other heat transfer surfaces.¹ Therefore, considerable effort has been expended to understand how alkali metals are partitioned during the coal combustion process.^{2–7} These studies suggest that, although organic sodium is vaporized during combustion, most of it reacts with aluminosilicates when these are present. The capture rate then increases with the temperature, resulting in less alkali-rich fume at higher temperatures.

This paper reports on a subset of results of a comprehensive study on deposit formation during the combustion of three coals, under both air- and oxy-fired conditions.^{8–12} A key objective of this study was to relate the size-segregated composition of the ash aerosol to the properties of the resulting deposits, gathered under controlled conditions, and to uncover differences (if any) between these for air combustion and oxy-combustion. The focus of this paper is different and uses previously unpublished results to quantify how sodium in coal influences deposit formation rates, which have rarely been measured under practical conditions. Previous work^{2,13} has attempted to correlate the net amount of sodium vaporized during coal combustion with the ratio of $\text{Na}/(\text{aluminosilicates})$ in the parent coal. It was thought that this should correlate with fouling propensity and, presumably, with rates of deposit formation. This idea can now be tested, for the first time in this paper.

2. MATERIALS AND METHODS

The experimental approach followed consisted of 16 tests on a 100 kW down-fired combustor, using associated deposit probes and aerosol sampling and measurement techniques. The furnace was the oxy-fuel combustor (OFC) that has been described in detail elsewhere.^{8,12,13} These studies differ from the smaller drop-tube studies in the literature, in that, here, combustion is self-sustaining and efforts are made to maintain temperature profiles, particle and gas species concentrations, and residence times similar to those in practical units while still maintaining the flexibility and cost of laboratory experimentation. It is hoped that this methodology allows for exploration of the pertinent mechanisms as they occur in field units, thus gaining systematic control of conditions without yielding relevance.

Another critical piece of equipment that was used here was a specially designed deposit probe, also described in detail elsewhere.⁸ An important feature of this probe is that the deposit coupon wall temperature was controlled (at 923 K in this work). For results reported here, the probe was always inserted at the same location (port 6), where, by happenstance, the flue gas temperature did not vary significantly from $\sim 1200\ \text{K}$, even though the peak flame temperature might vary by over $\sim 200\ \text{K}$, depending upon the input conditions.

One characteristic of this combustor/deposit probe system is that the flow in the post-flame near the deposit probe is necessarily laminar, and therefore, to be extrapolated to field conditions, the measured

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deposition rates require modeling the aerodynamics of the deposition process. However, measured differences in rates, mechanisms, and effects of variations in the ash aerosol caused by changes in fuels and combustion conditions upstream should be transferrable to field units. It is from this perspective that the role of sodium in coal in determining deposition rates is explored here.

Deposit samples collected on the coupon can be divided into two types: (1) tight, sticky “inner” deposits that strongly adhere to available surfaces, especially to the heat transfer surfaces, and (2) loose “outer” deposits that are easily dislodged and potentially re-entrained by the flue gas. From a practical point of view in these experiments, the loose “outer” deposits are designated as those that are easily dislodged by vigorous shaking and the sticky “inner” deposits are those that remain attached and can only be removed by scraping the surface of the deposit probe. Precise measurements of deposit rates may be made only of the tight, sticky “inner” deposits, because these are not sensitive to re-entrainment by flue gases and to being lost during extraction of the deposit probe. Measured deposition rates reported in this paper are, therefore, those only for the tight “inner” deposits and were taken from deposition holding times of 1 or 2 h. Previous research showed significant distinctions between the “inner” and “outer” fouling deposits in both physical (such as particle size) and chemical (such as elemental composition) properties, which implies different formation mechanisms. A detailed description of the approach and the analysis of the inside and outside deposits could be found elsewhere.⁸

Ash aerosol particle size distributions (PSDs) were obtained using an isokinetic, water-cooled, quenched (at the tip) dilution probe. The sample could then either pass through a cyclone and an 11-stage Berner low-pressure impactor (BLPI, for particle diameters of 0.0324–15.7 μm) or undergo a second dilution and pass through an online TSI scanning mobility particle sizer (SMPS)–light-scattering aerosol particle sizer (APS) duo, to allow for measurement of PSDs between 0.0143 and 0.672 μm (SMPS) and between 0.532 and 20 μm (APS). The aerosol sample probe was inserted downstream of the deposit probe, but equilibrium calculations suggested that little was likely to change the ash aerosol composition between these two locations. A Mettler pico-balance allowed for accurate weights from the BLPI stages to be obtained, allowing for gravimetric PSDs to be compared to electric-mobility and light-scattering PSDs.⁹ Collected samples from the BLPI stages were chemically analyzed for elemental composition by energy-dispersive X-ray spectroscopy (EDS).

Deposition rate data were obtained for a total of 16 tests shown in Table 1. These test conditions were originally determined to examine the effects of various oxy-firing configurations on the ash aerosol and deposit properties. This was not an experimental test matrix devised to

examine the effect or role of sodium, because questions relating to this particular issue appeared only after the tests were completed and the data were analyzed, as will be apparent below. Deposition rates for the inside, sticky deposit were obtained for the PRB coal burned in air, in an inlet mixture containing 73% CO_2 /27% O_2 (denoted as OXY27) and with an inlet mixture containing 50% CO_2 /50% O_2 (denoted as OXY50). Once through, CO_2 was used for cases 2 and 7 (PRB coal). For the other oxy-combustion cases, dilution was accomplished by recycling the flue gas with either just the ash removed (denoted as ash), ash and water removed (denoted as ash_ H_2O), or ash, water, and SO_2 removed (denoted as ash_ H_2O _S). Case 6 used recycled flue gas with nothing removed (denoted dirty). The deposit collection probe surface temperature was controlled at 923 K ($T = 923$), and the deposits were collected from port 6 of the furnace.^{8–12}

Properties of the suite of coals examined are shown in Table 2. The coals were an Illinois bituminous, a Powder River Basin (PRB) sub-bituminous, and a 60:40 blend of Illinois/PRB (blend), similar to what had been planned for FutureGen 2.0. This suite allowed effects from major differences in moisture content, heating value, sulfur content, calcium, and iron to be examined. The sodium content did not vary over a wide range, although silicon and aluminum contents did. The ratio of $\text{Na}/(\text{Si} + \text{Al})$ was that of the oxides, as reported in the ash analysis.

3. RESULTS AND DISCUSSION

3.1. Relationship between Vaporized Sodium and the Ratio of Acid-Soluble Na/Aluminosilicates in the Fuel

Previous work on partitioning of sodium has focused on determining how much of the sodium was vaporized, where the fraction vaporized was taken to be the fraction of total sodium that was collected as particles with an impactor d_{50} of $\sim 0.6 \mu\text{m}$.^{2,13} It was hypothesized that the net fraction vaporized depends upon the organic sodium content and the aluminosilicate (Al–Si) content, where an increased combustion temperature increased the scavenging by aluminosilicates and, hence, decreased the sodium as vapor. The old data on Figure 1 show data from U.S. coals, from the Australian Loy Yang coal, which had low ash, nearly all of which was organic sodium, and data from experiments in which the fuel was doped with either kaolinite (to increase Al–Si) or sodium acetate to increase Na^2 . The oxy-combustion data of Morris et al. has been added,¹³ and to all of this, the new data from this project has also been added, as shown on Figure 1. Alas, the new data (PRB, Illinois, and blend) did not improve the correlation, although the slope with respect to the abscissa was similar. The fraction of sodium vapor was generally lower than the previous literature data. This might be due to the increased temperature in some but not all of the experiments in this work. The measured peak gas temperatures (using unshielded thermocouples) for the PRB OXY50 runs were 200 K higher than those for PRB air.

3.2. Measured Inside Layer Deposition Rates Versus $\text{Na}/(\text{Al} + \text{Si})$ in the Parent Coal. Results describing inside layer deposition rates are shown in Figures 2–5, where the error bars shown reflect the variations between measurements from three repeated tests.

Because Figure 1 was originally developed with a view to being able to predict deposition rates, it seemed reasonable to check the relationship between measured deposition rates (for the inside layer on the deposit probe) and the ratio of $\text{Na}/(\text{Al} + \text{Si})$ in the coals of this study. These data are from the 16 cases denoted on Table 1 and described above. Results are shown in Figure 2.

If the four PRB OXY50 points are excluded, the correlation appears to be quite good. However, the fact that all PRB

Table 1. Test Cases for Which Deposition Rate Data Were Obtained^a

case 1	PRB, air, port 6, $T = 923$	△
case 2	PRB, OXY27_once, port 6, $T = 923$	△
case 3	PRB, OXY27_ash, port 6, $T = 923$	△
case 4	PRB, OXY27_ash_ H_2O , port 6, $T = 923$	△
case 5	PRB, OXY27_ash_ H_2O _S, port 6, $T = 923$	△
case 6	PRB, OXY27_dirty, port 6, $T = 923$	△
case 7	PRB, OXY50_once, port 6, $T = 923$	▲
case 8	PRB, OXY50_ash, port 6, $T = 923$	▲
case 9	PRB, OXY50_ash_ H_2O , port 6, $T = 923$	▲
case 10	PRB, OXY50_ash_ H_2O _S, port 6, $T = 923$	▲
case 11	Illinois_air, port 6, $T = 923$	□
case 12	Illinois_OXY27_ash, port 6, $T = 923$	□
case 13	Illinois_OXY27_ash_ H_2O _S, port 6, $T = 923$	□
case 14	blend_air, port 6, $T = 923$	◇
case 15	blend_OXY27_ash, port 6, $T = 923$	◇
case 16	blend_OXY27_ash_ H_2O _S, port 6, $T = 923$	◇

^aSymbols are those used in Figures 1–5.

Table 2. Coal and Coal Ash Compositions

	coal analysis			coal ash analysis			
	Illinois	PRB	blend		Illinois	PRB	blend
ash (%)	9.42	4.94	7.63	Al ₂ O ₃ (%)	20.18	14.78	18.02
C (%)	63.47	53.72	59.57	CaO (%)	3.22	22.19	10.81
H (%)	5.43	6.22	5.75	Fe ₂ O ₃ (%)	16.46	5.2	11.96
N (%)	1.24	0.78	1.06	MgO (%)	0.89	5.17	2.6
S (%)	3.12	0.23	1.96	MnO (%)	0.03	0.01	0.02
O (diff) (%)	17.32	34.11	24.04	P ₂ O ₅ (%)	0.1	1.07	0.49
LOD (%)	9.64	23.69	15.26	K ₂ O (%)	2.1	0.35	1.4
V (%)	36.04	33.36	34.97	SiO ₂ (%)	51.22	30.46	42.92
FC (%)	44.9	38.01	42.14	Na ₂ O (%)	1.06	1.94	1.41
HHV (BTU/lb)	11552	9078	10562	SO ₃ (%)	2.79	8.83	5.21
				TiO ₂ (%)	0.98	1.3	1.11
				Na/(Si + Al)	0.0148	0.0429	0.0231

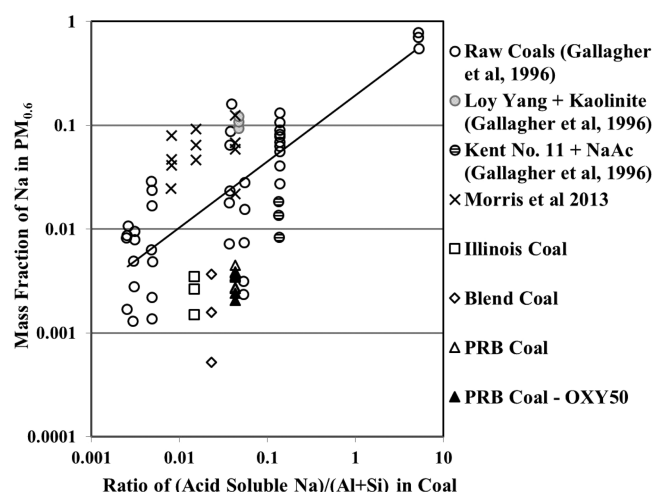


Figure 1. New and literature^{2,13} data on the fraction of sodium vaporized versus (acid-soluble Na)/(Al + Si) in the fuel. The abscissa is actually acid-soluble Na₂O/(SiO₂ + Al₂O₃) in the parent coal. This figure is plotted by adding new data points into published data in the literature. Acid-soluble Na reported by Gallagher et al.² is sodium that could be extracted by ammonium acetate solution. For the three new coals added to this figure, it was assumed that all sodium was acid-soluble. Morris et al.¹³ used the same PRB sub-bituminous coal as in this work, a Utah low-sulfur bituminous coal, and an Illinois high-sulfur bituminous coal and also assumed that all sodium was acid-soluble.

OXY50 are bunched together, lying outside of the other data, suggests that this anomaly should be explored in more detail.

3.3. Measured Inside Layer Deposition Rates and PM₁ Compositions and Concentrations in the Flue Gas. Sodium vapor and its subsequent nucleation and condensation to form “sticky” surfaces have been identified as contributors to fouling and, presumably, to formation of the inside deposit layer. Indeed, that has been the motivation for the correlation shown in Figure 1, in the hope that fouling rates can be predicted from knowledge of the sodium and aluminosilicate contents of the fuel.

Because condensation causes enrichment on the smaller ash particles because of increased surface/volume ratio, it seemed logical to explore correlation between measured deposition rates and the sodium content of PM₁ and PM_{0.6}. Results from the 16 tests depicted on Table 1 are shown for PM₁ in Figure 3 and for PM_{0.6} in Figure 4.

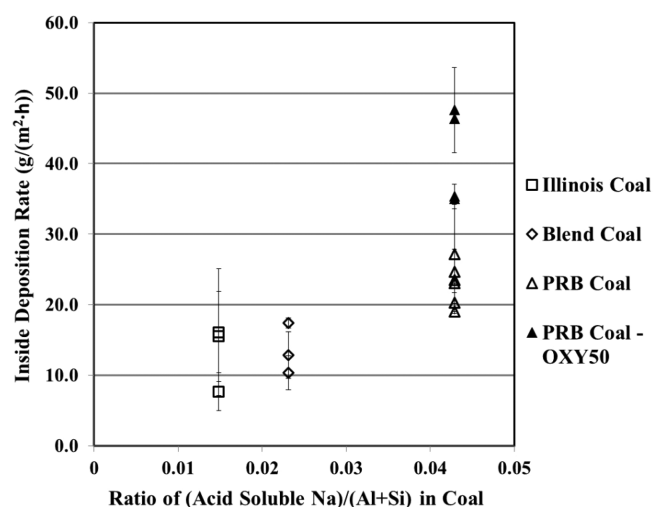


Figure 2. Measured deposition rate for the inside layer versus ratio Na/(Al + Si) in coal.

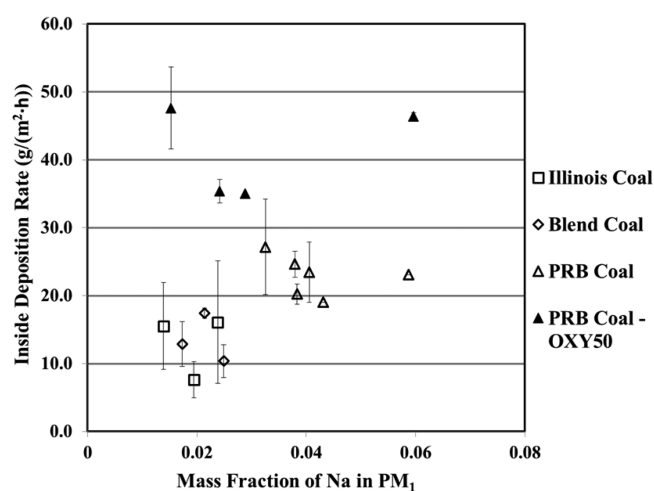


Figure 3. Deposition rate of the inside deposit layer versus sodium content in ash particles with diameter (d_{50}) less than 1 μ m (PM₁).

A cursory glance at Figure 3 suggests that the correlation is not good, which seems to conflict with possible conclusions to be drawn from Figure 2. However, if one neglects (for the moment only) the four data points representing deposition rates for the PRB50, one sees that a correlation exists for both

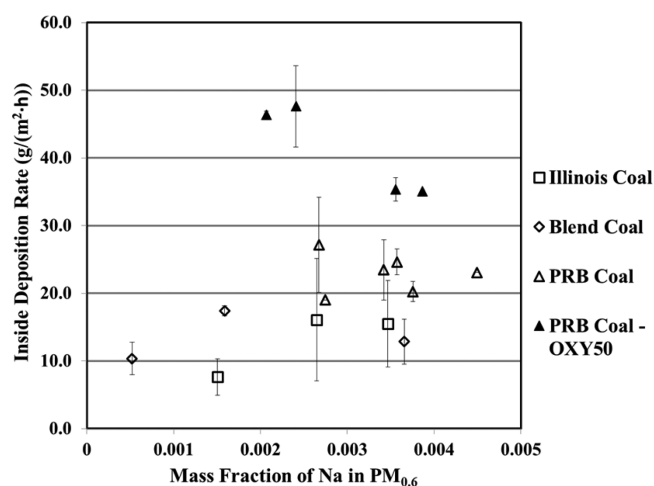


Figure 4. Deposition rate of the inside deposit layer versus sodium content in ash particles with diameter (d_{50}) less than $0.6 \mu\text{m}$ ($\text{PM}_{0.6}$).

Figures 3 and 2. This suggests that deposition rates can be correlated with sodium vaporization and, hence, sodium content in coal, provided that it creates a significant concentration of sodium in PM_1 . Where sodium is not present in a significant amount in PM_1 , high deposition rates are still possible, and these do not correlate with sodium in PM_1 or in the coal.

The sodium content of $\text{PM}_{0.6}$ (Figure 4) does not change these conclusions. High deposition rates can be achieved without high concentrations of sodium in the ultrafine ash particles.

Figures 2–4 suggest that, although sodium content in the deposited ash is the controlling variable for some of the data, it is not for all of the data. Indeed, the highest deposition rates have been observed where there is evidence of lower sodium vaporization, i.e., lower concentrations of sodium in PM_1 and $\text{PM}_{0.6}$.

Previous research showed that the inside deposits mainly consisted of fine and ultrafine particles and the compositions of the inside deposits and PM_1 are similar.¹⁰ Therefore, because the sodium content alone did not appear to be the best correlating variable for deposition rates, it was decided to use the concentration in the flue gas of all particles comprising PM_1 . In Figure 5, deposition rates (inside the deposit layer only) are correlated with the overall concentration of PM_1 in the flue gas, for all of the deposition rate data collected. The correlation is excellent, with no exceptions. Note the high deposition rates for the PRB OXY50 runs that failed the previous correlations but fitted this one. These had high flame temperatures (50% O_2 input), lower sodium contents in the sub-micrometer particles (increased sodium scavenging), but increased silicon contents (increased silicon vaporization). The actual compositions of the size-segregated ash aerosol and those of the resulting deposits have been published by Zhan et al.¹² Overall, this work shows that the inside fouling deposition rate is related to the concentration of PM_1 , instead of the chemical composition, such as the content of Na. This viewpoint has been proposed for the first time and differs from the traditional viewpoint. Additional research to confirm this would be useful, and it is within the future research scope of this research group.

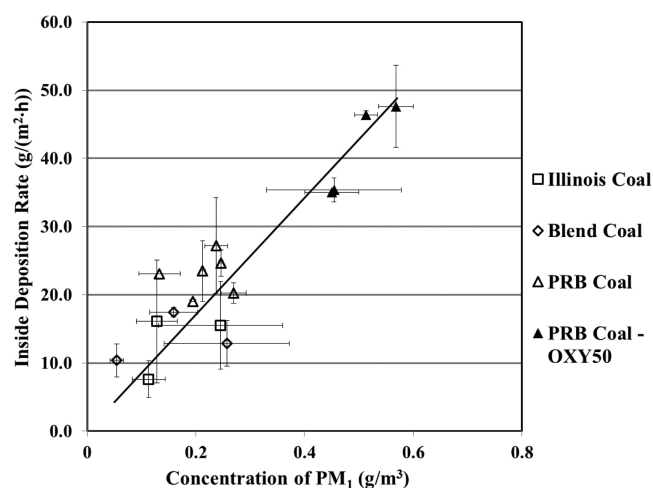


Figure 5. Correlation of measured deposition rates (inside deposit layer) versus PM_1 , regardless of the composition of PM_1 .

4. CONCLUSION

Data suggest that the primary mechanism determining the rate of formation of the inside, firm, layer of the deposit is deposition of sub-micrometer particles, of any composition. This conclusion is reached from consideration of all of the deposition rate data obtained from 16 tests involving three coals and a range of oxidants. Although no exceptions to this conclusion were uncovered in this study, it would be prudent to confirm the generality of this result through additional experiments involving high-sodium coals, such as the Australian Loy Yang or the high-sodium Beulah lignite, or biomass and biomass/coal blends burned under a wider range of conditions. It should be emphasized that this conclusion does not relate to slagging rates, which were not measured here and were outside the scope of this work.

Within a sub-range of PM_1 flue gas concentrations, the sodium content in the coal or rather the $\text{Na}/(\text{Al} + \text{Si})$ ratio may control these deposition rates. The data show that the sodium content in the fuel is important in determining PM_1 but that it may not be the only factor or even the main, especially at high flame temperatures (e.g., PRB OXY50), where sodium vapors are scavenged by larger particles and silicon vaporization is enhanced. One cannot rule out, however, that small amounts of sodium may still play a critical role by coating the silicon-rich sub-micrometer fume with a thin layer of sodium.

The fact that deposition rates correlate so well with PM_1 no matter what the PM_1 composition may be is important because it suggests a possible method for online measurement of deposition rates using online measurements of PM_1 , by a SMPS for example. Online composition measurements are not required. The results of this work also suggest that deposition simulations pay attention to PM_1 formation rates rather than focusing exclusively on stickiness and viscosity predictions.

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Notes

The authors declare no competing financial interest.

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