

Studies of the Release of Sodium from Pulverised Coal in a Flat Flame Burner

By

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Abstract

This paper investigates the problem of the rate of release of alkalis from coal/coal blends as they are burnt in Utility Boilers with the aim of evolving better models of the effect of given fuel blends on slagging and fouling in real boiler situations. Although numerous slagging and fouling indices have been evolved over many years to describe the behaviour of coals in given boiler situations they often fail to give the required results and prove to be of little use when co-firing blends of coal with biomass materials.

In this work we have constructed a natural gas flat flame burner with associated furnace and viewing ports so we can use a PLIF system to look at the evolution of sodium from burning coal/coal blend particles and relate this to the condition of the ash in the burning coal particle as the ash particle reaches the region of the superheater tubes in a boiler. By appropriate adjustment of the air fuel ratio we can produce temperature/residence time distributions downstream of the flat flame burner and in the furnace section which closely parallel those found in Utility Boilers. Pulverised coal particles as produced for boiler firing are sieved into two fractions, those in the size range 67 to 37 microns and above 67 microns (virtually no residue was found below 37 microns). This was to ensure that the finer fraction had a narrow size distribution, which devolatilised and burnt in a time frame commensurate with that of our system

Particle velocities could be readily measured by streak velocity using the available PLIF camera via their radiation signal produced from their combustion process. The camera was aligned such that the initial devolatilisation process was not observed as the associated radiation could mask the PLIF image; this proved to be satisfactory as significant sodium evolution did not occur until after the end of the devolatilisation process. PLIF images of the sodium evolution were generated via excitation of the D₂ line at 16960.95 cm⁻¹ with collection via a gated intensified CCD camera (Princeton Instruments ICCD-576). Four groups of images (500 images per set) were generated and collected at each setting to ensure accuracy of results, with a polarisation filter to minimize interference from Mie scattering with the sodium fluorescence.

Novel results have thus been produced which will allow the evolution of better models for predicting slagging and fouling, especially when the work is extended to other volatile species in coal ash.

Introduction.

This paper discusses a novel technique for analysing emissions of sodium and eventually other species of interest from pulverised coal and pulverised coal/biomass fuel mixes as at present being burnt in large power station boilers. At present there are a number of well-known coal indices that are routinely used to predict the slagging/fouling propensities of coals/coal blends that are routinely fired in large power station boilers. These indices include the silica ratio, base/acid ratio, iron/calcium ratio, silica/alumina ratio and various empirically based slagging factors based on either measurements of temperatures producing a given ash viscosity or the softening/melting behaviour of ash samples. With the increasing trend for boiler co-firing with a wide range of alternative materials, broadly classified as biomass at substitution levels up to 5% by heating value (often 10% by weight) existing indices are proving to be inadequate to successfully predict the fouling/slagging behaviour of these new fuel mixes. One of the characteristics of many biomass materials is the presence of significant quantities of easily volatilised alkali and other salts in the ash that can radically alter the characteristics of the ash and how it deposits on heat transfer surfaces. Other problems can include the presence of heavy metals from various wastes and how they affect the fouling/slagging in a given boiler.

Of course each boiler tends to have different characteristics and it is not economic to perform full CFD analysis of the system; indeed although CFD codes are becoming increasingly accurate in their

predictions of combustion performance there is still an enormous gap in their propensity to predict slagging and fouling differences between different fuel blends. The reason for this lies in the lack of understanding of how the various ash constituents bound in the coal/fuel matrix behave as they pass through the time/temperature conditions found in the specific boiler.

This paper thus starts to address part of the issues involved by looking at the evolution of volatilised sodium from pulverised coal particles heated in a natural gas fired flat flame burner, designed to produce a time/temperature history very similar to that occurring in the first section of large pulverised coal fired boilers. The intention is, once the technique is fully proven, to extend it to a range of other elements of interest including, potassium, copper, iron, lead, phosphorus etc. The intention is to couple these results with available software, like Factwyr (a well known chemical database and analysis package), which enables predictions to be made of volatilisation rates of elements, compounds etc at specific temperatures and time regimes, thus enabling estimates to be made of the condition of ash particulates and their propensity to stick to surfaces. Another important aim is the characterisation of ultra fine particles, especially those < 1 to 2 microns, as it is these that can cause lung damage and bypass many dust collection systems. Many of these arise from condensation processes from vapourised constituents of the ash

Apparatus

The flat flame burner was manufactured from 216 hypodermic tubes of internal diameter 1.17mm, outer diameter 1.76 mm. 72 bundles of 3 tubes, in the form of equilateral triangles, were then formed into a burner matrix 51 mm by 53 mm square, each bundle of three tubes being separated by 5.7 mm. This was then surrounded by a brass containment vessel. The length of the hypodermic tubing was 80 mm and gases were fed into these tubes via a plenum chamber which was fed off the side wall. This was fed with premixed natural gas and air, the natural gas originating from the mains at Adelaide University, the air from the main compressor. Just before the premixer for the air and natural gas the compressed air was fired through a calibrated ejector which sucked and then compressed small quantities of ambient air into the unit. This allowed the feeding of small quantities of pulverised coal and/or other materials into the line and system so that these particles would be heated up to appropriate conditions in the flat flame burner and thus the emissions of sodium tracked. Calculations, observations and measurements of the resulting flame indicated that it was laminar and one dimensional in the central region of flow.

Attached to the top of the burner was a small 600 mm long refractory lined furnace, whose internal dimensions matched the 51 by 53 mm dimensions of the burner. A small 5 mm wide slit was cut along the middle of the 53 mm sides to allow access for the laser sheet and prevent reflection from the opposite wall. Eventually to allow successful operation of the PLIF system both front and back walls of the furnace for the first 300 mm of the furnace length had to be removed to prevent excessive flare from the high temperature refractory obliterating the PLIF signal. This in fact matched the size of the laser sheet quite well. It was however necessary to retain the downstream walls of the furnace on all four sides in order to be able to develop the desired time temperature profile to match that found in the initial stages of large Utility Boilers. Photographs of the rig are shown in figure 1 below illustrating the long slit to allow access for the laser sheet and the rig operating on natural gas whilst burning fine coal particles. The whole rig could be vertically traversed to increase the measurement range.

The coal was American Peabody with the following inorganic analysis, Table 1 below:

HRL Sample ID CMM/04/255 No.	Sample Identification	Si	Al	Fe	Ti	K	Mg	Na	Ca
1	Peabody	1.69	0.88	0.90	0.048	0.077	0.04	0.06	0.29

Table 1 Inorganic Analysis of the Ash in the Peabody test Coal (% Dry Basis)

Sodium levels are quite low, being 0.06% in the ~ 4% ash content of the coal. Thus sodium is about 1.5% of the total inorganic ash content, quite a low figure and depletion effects should be expected as the coal particles heat up to the 1300°C/1400°C level.

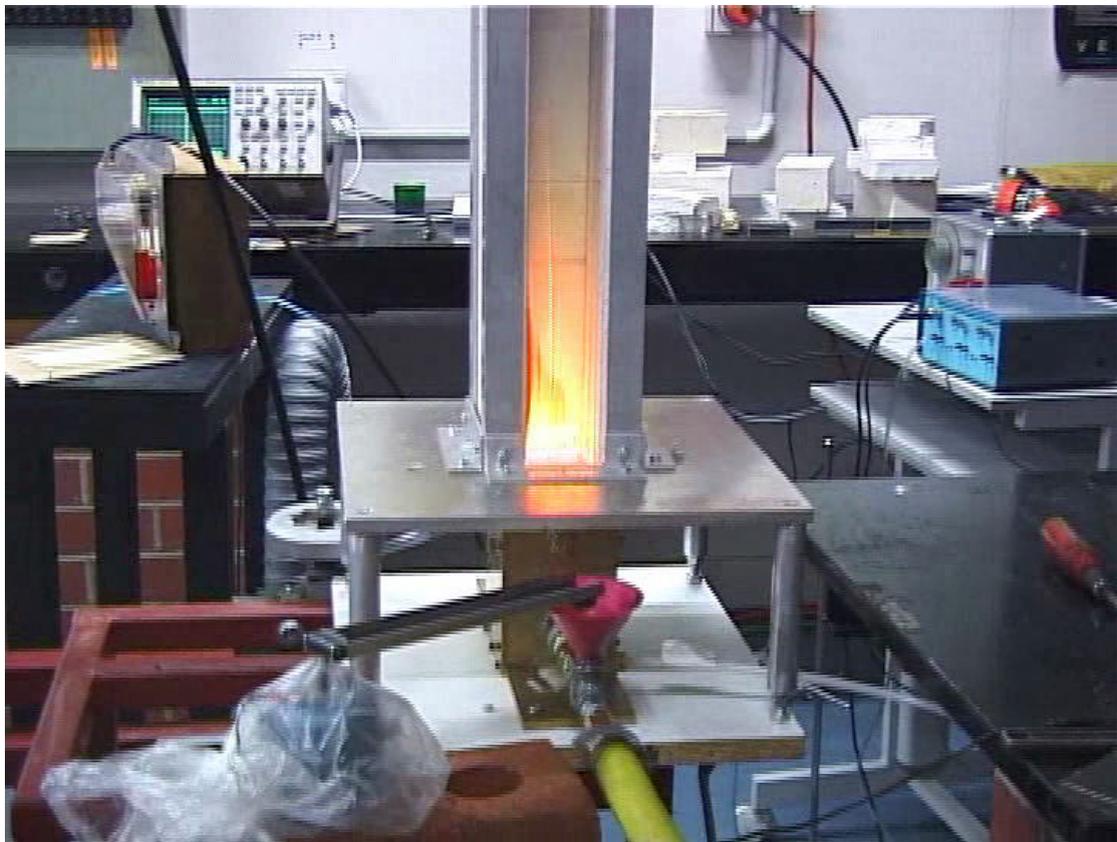
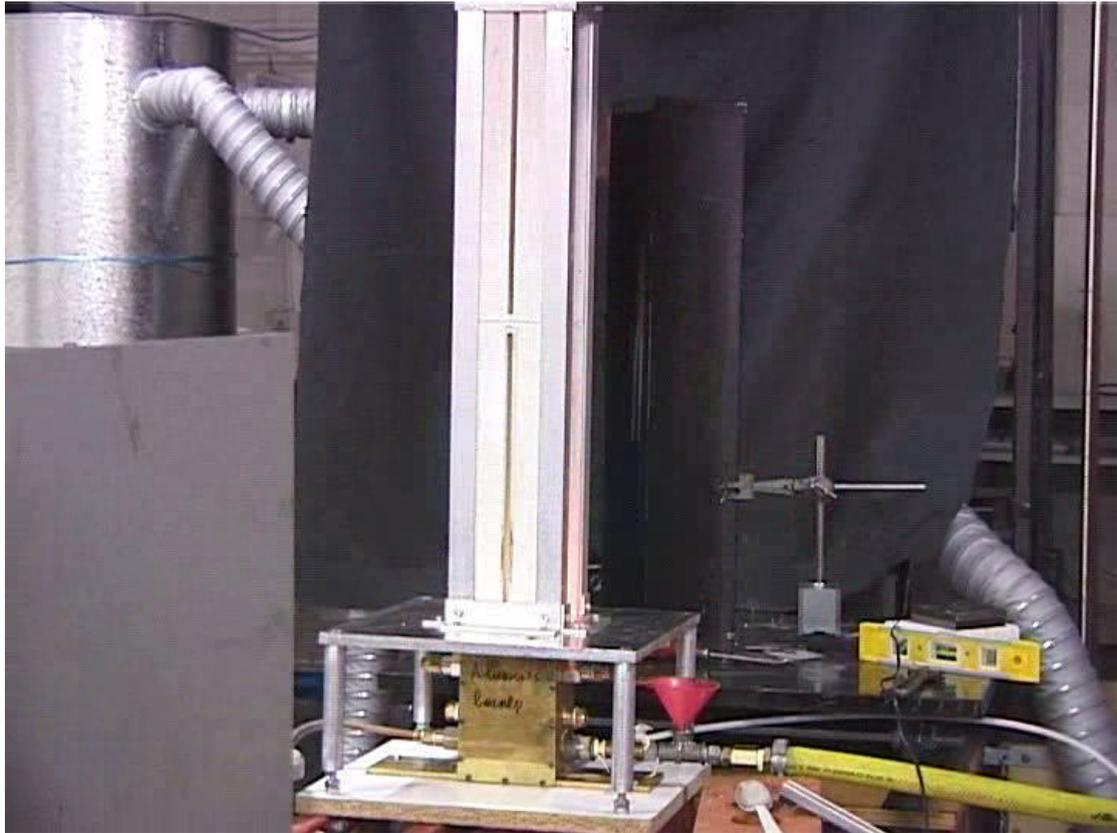


Fig 1 Views of Rig showing slit for laser sheet (top) and the rig burning coal (bottom)

Instrumentation

Two-dimensional images were obtained using PLIF (Eckbreth, 1996) with the set-up as shown in Figure 2. A tuneable dye laser (Quantel, TDL90), pumped by a Nd:YAG laser (Quantel, YG980), was used as the excitation source. The tuneable output from the dye laser is specified to have a line width value of $\sim 0.08 \text{ cm}^{-1}$. The output radiation was directed to appropriate cylindrical and spherical lenses to form a sheet of light. The sheet was relatively uniform over the 100mm height and 50mm width of the image. In any case measurements are only reported from the centre line of the furnace. The light sheet thickness was estimated to be $\sim 1 \text{ mm}$. A small part of the laser beam was sent to a pulsed wavemeter (Burleigh 5500) for absolute wavelength calibration.

The dye laser was scanned around 16970 cm^{-1} to excite the D_1 and D_2 Na lines at 16978.22 cm^{-1} and 16960.95 cm^{-1} , respectively. All the measurements were performed using the D_2 line as strong beam absorption was observed when using the D_1 line. The maximum energy of the pump beam was $\sim 8 \text{ mJ}$ per pulse. The pulse-to-pulse energy jittering was measured to be about 15%. Measurements began about 10 to 15 mm above the exit of the burner as temperature measurements indicated it was in this region that highest temperatures were reached and the particles had devolatilised. Particle size was carefully controlled by sieving the coal so that all material above 67 microns was removed; little was found below 30 microns. Typically the average size was 50 microns and this was carried out to reduce

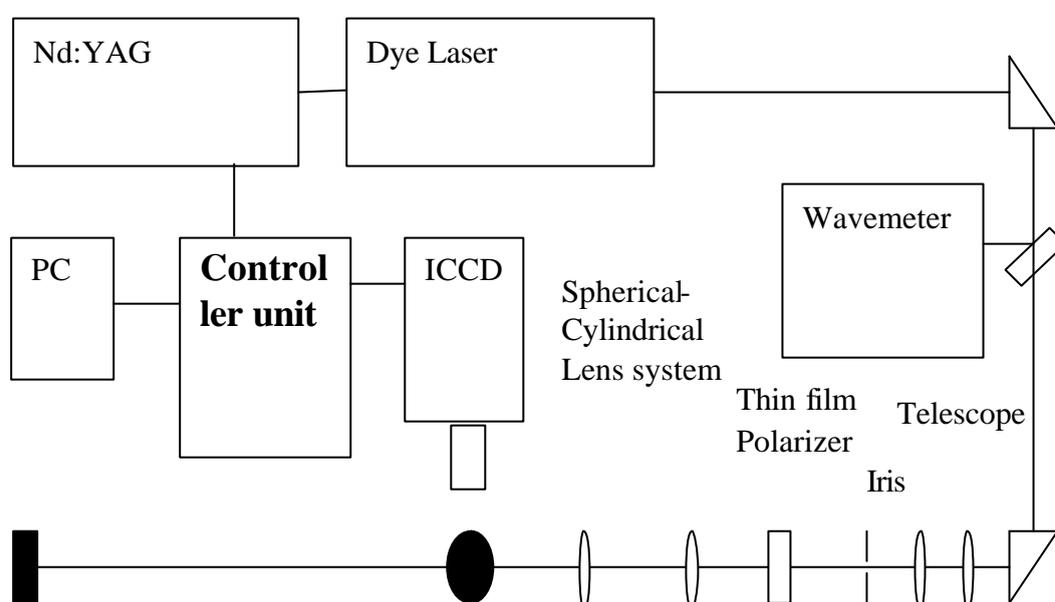


Figure 2: A schematic diagram of the experimental arrangement.

the variation in burning time as much as possible and prevent mie scattering from burning volatiles interfering with the measurements.

The laser-induced fluorescence signal from the Na atoms was collected using a gated intensified CCD camera (Princeton Instruments ICCD-576) orthogonal to the laser sheet. A gate width of 100 ns was selected to minimise background radiation from the flame. When the dye laser was tuned to 16960.95 cm^{-1} a strong PLIF signal was observed. Several hundred images were recorded after ignition with 10 images collected at 10Hz every ten seconds. A background subtraction was applied to all images followed by a correction for the axial variation in light sheet intensity. A polarisation filter was also used to minimise mie scattering from the particles

An extremely useful feature of the rig was that the once the particles had devolatilised and the associated long tail of burning volatiles had disappeared the particles still glowed as they burnt in the

hot gases. Thus by readjustment of the camera streak images of the coal particles motion could be obtained, thus translated to velocity and hence residence time in the system.

The temperature profile on the centre line of the flat flame burner/furnace system was characterised by means of bare wire fine Pt/Pt-13%Rh thermocouples for a number of relevant cases whilst firing just natural gas and air.

Previous work

The only known previous work to that presented here is that of Nathan et al (2003), who used the same PLIF system, applied it to a standard and dewatered Loy Yang Australian coal, but using particles of about 3.5 mm in diameter heated in the tip of a Bunsen burner and supported by a ceramic rod. One set of samples was from untreated brown Loy Yang Coal, the other from treated and dewatered Loy Yang, termed MTE after the processing to remove water. The time variation of sodium emission over 900 seconds was studied as the coal particle devolatilised and burned. Results are shown in figure 3 below for the pure and MTE coal, weights of each sample are shown on the figure. Not surprisingly the signal intensity from the pure Loy Yang coal is approximately twice that of the dewatered, processed MTE coals, (where about 50% of the sodium has been removed), the plume also being slightly larger. These differences are clear from Figure 3 which shows the integrated signal from each coal as a function of time. Each data point is averaged from ten images and integrated over the entire plume. There is some scatter in the individual data points. This can be attributed to the combined effects of an observed puffing motion and to more rapid temporal variations in the actual emissions due to the inhomogeneous nature of the fuels. Nevertheless, a clear trend is apparent in each data set, revealing the following features. Within a few seconds from the time when the Bunsen burner is lit, a strong initial peak in the signal is found. This signal rises to its peak and decays again to background levels within about 20 seconds. This initial peak is deduced to correspond to the Mie scattering signal from the soot emissions associated with the initial period of devolatilisation. The Mie scattering signal from the soot was not directly distinguishable from the PLIF signal because they are at the same frequency (and gave rise to the use of a polarisation filter in the present work). That this initial plume is associated with the presence of soot is evident from visual observation of the highly yellow colour of the flame, which contrasts markedly from the subsequent pale orange colour associated with the Sodium. It is significant that the sodium emission does not begin until after the presence of soot is no longer evident, some 30-40 seconds after the particle is ignited, and does not peak until 200 – 300 seconds after ignition. A signal from Na is still present up to 900 seconds after ignition. At that stage the signal is still higher than the back-ground emission associated with the ceramic rod, but is sufficiently weak to suggest that most of the sodium emission is complete.

Several other important issues can be deduced from figure 3. Firstly, there is a significant difference in the total amount of sodium emitted from the different coal types. Secondly there is also substantial variation in the emission from different samples of the same coal. The sample-to-sample variation in a given coal is well known and the present sample size is clearly too small to allow any statistically significant comparison in total relative emissions. However there appears to be less variation in the time between the ignition and the peak emission than in the magnitude of the signal.

In the context of the present work it is useful to compare the time scales of the various processes occurring as follows:

- Devolatilisation : complete by about 33 seconds for all coals
- Maximum emission of sodium occurs for the pure Loy Yang coals over 250 to 400 second range

Scaling this to 50 micron coal particles (via the normal diameter squared burning law for burning time) gives for a particle scale factor of 70 (3500/50 microns):

- Devolatilisation time ~ 6.7 milliseconds (in the expected range for 50 micron particles)
- Maximum emission of sodium thus expected to occur in the 50 to 80 millisecond time frame for the same heating conditions. However differences are to be expected in the emission times for sodium as the temperature residence time distribution is somewhat different for Nathan et al (2003) as the larger particles are held at a given point in a flame and subjected to essentially the same temperature environment for 900 seconds. Moreover as the large coal particle was held in an open flame, significant radiation heat losses will have occurred and temperatures will be significantly lower than in the flat flame furnace. In the present work the particles are subjected to a carefully controlled time temperature history analogous to that found in the initial section of large Utility Boilers. Here expected burnout time for 50 micron coal particles are expected to be in the range 10 to 30 milliseconds.

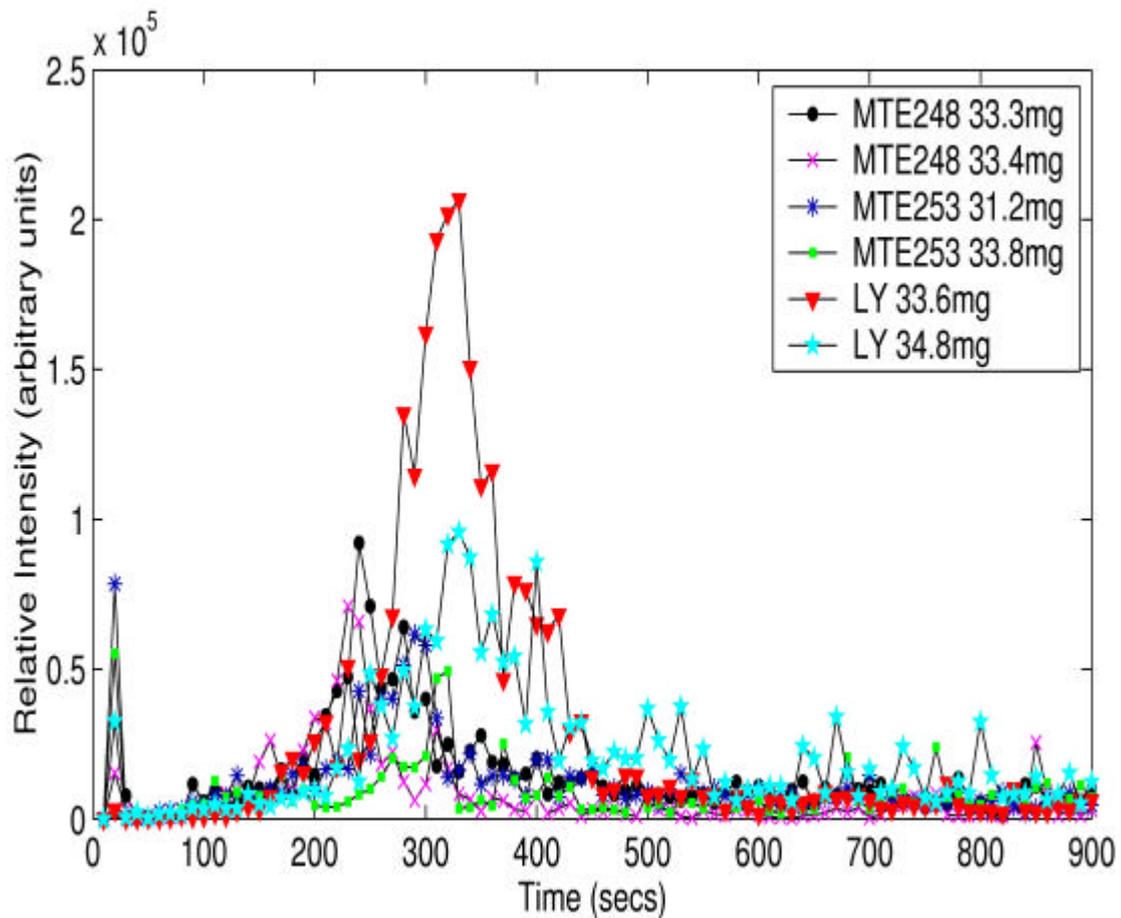


Figure 3: The temporal variation of total Na emission for the three types of coal.

In the context of slagging and fouling of large boilers the interest thus is when in the devolatilisation/char combustion process in the coal particle does the sodium start to be evolved in significant quantities as this (together with information on the evolution of other species to be hopefully gathered in the future) will then enable detailed analysis to be made of:

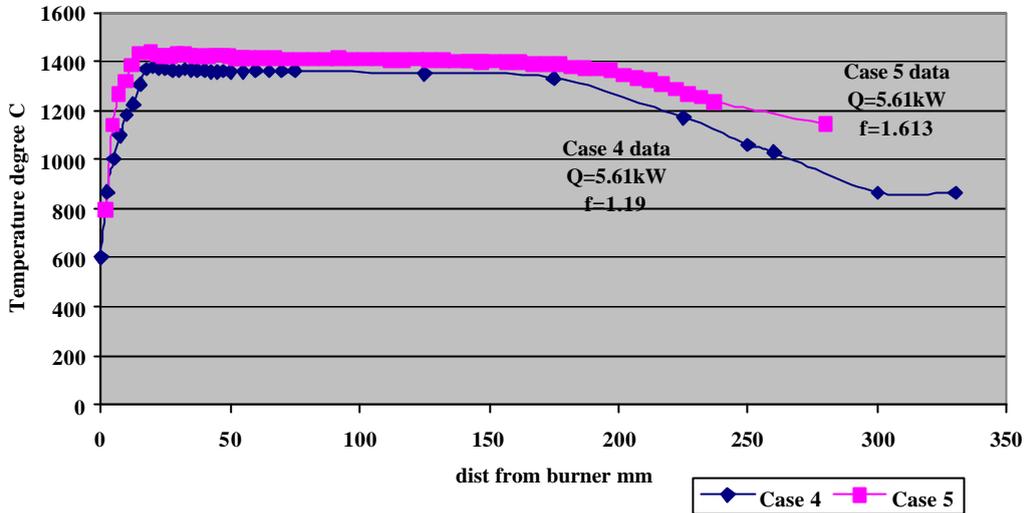
- The condition of the particle, its temperature and via software like Factwyn, make determination of the propensity for it to stick to given heat transfer surfaces
- Make estimates of condensation processes later in the boiler which can give rise to ultra fine particulates

Results

Initially the rig has been operated in a number of conditions, air/natural gas ratios to explore its range of operation especially with respect to the time temperature history. This is illustrated below in Fig 4, which shows the centreline temperature distance as a function of axial downstream distance for 2 cases, each with a thermal input of 5.61kW, but with different equivalence ratios. Each case is fuel rich as it leaves the burner nozzles and fuel burnout occurs as air is entrained from the two open sides of the furnace. This has the advantage that the coal particle is exposed to an initially fuel rich environment analogous to that found with low NO_x burners. As can be seen after the exit of the burner temperatures rise rapidly to 1000°C within 5 mm of the burner exit and exceed 1300°C within 15 mm. Maximum temperatures achieved are just under 1400°C and just over 1400°C for cases 6 and 5 respectively. Most importantly these temperatures are very much maintained for nearly 200 mm in both cases, giving high temperature residence times of order 20 to 30 milliseconds for particles. This occurs because the flames are initially fuel rich and entrain air from the open two sides of the furnace thus maintaining combustion over a longer section and similarly maintaining temperature, whilst producing conditions analogous to those found in the first stage of low NO_x burners. The residence time is adequate for the

50 micron mean sized coal particles used and certainly enables the first stages of the sodium evolution to be studied. Moreover as the calculations in the section above indicated devolatilisation was found to be rapidly completed so it did not interfere with the PLIF measurements. This was not the case with larger coal particles as found using unsieved pulverised coal, where burning volatile trails could be clearly discerned behind larger particles.

Fig. 4. Temperature Profiles along Flat Flame Furnace



Inevitably the furnace is a compromise in allowing access for the laser sheet and the camera without encountering significant flare and problems with signal to noise ratio with the PLIF signal. Figure 5 below shows the average PLIF sodium signal from an n American Peabody coal as a function of downstream distance. Figure 6 shows a comparison of the centreline intensity, mean measured temperature for this case, and corresponding mean particle residence time obtained separately from the particle streaks. Maximum intensity of the LIF signal is obtained at an axial distance of ~ 180 mm, corresponding to a residence time from the burner exit of 20 milliseconds. Close to the burner there is still some mie scattering effect from the burning volatiles and this correlates with the temperature profile, Figure 4, where maximum temperature was reached at about 18 to 20 mm above the burner. Thus the volatiles from the coal are burning out by about 70 to 80 mm above the burner, corresponding to a residence time of about 9 milliseconds, consistent with known data.

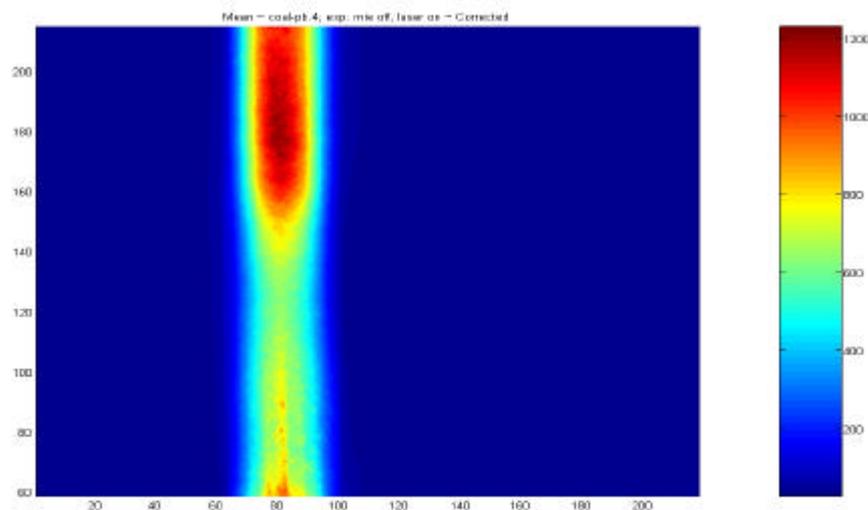


Figure 5 Average of 500 Images PLIF Na Signal

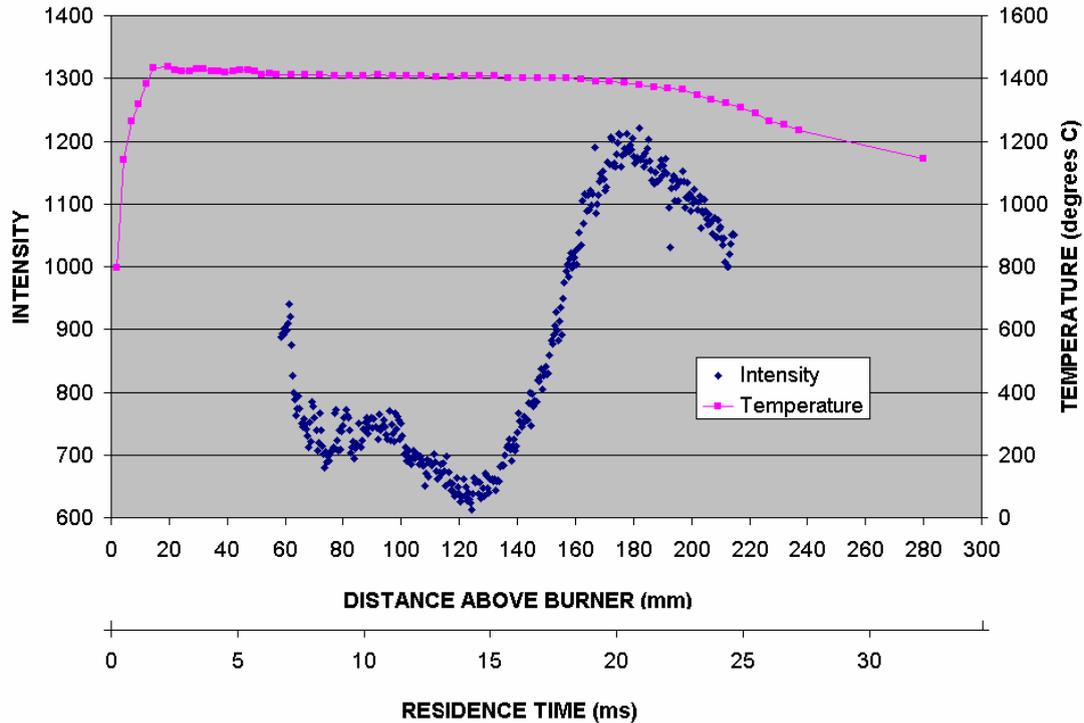


Fig 6 Comparison of the Mean Centreline Temperature, LIF Na Intensity Signal with Axial Distance and residence Time

The LIF intensity curve shows several other interesting features besides the peak at 180 mm or 20 milliseconds residence time, as after this position there is a very sharp fall off in LIF intensity.

Figure 7 a, b, c and d show four individual images from the 500 collected in this study of one coal. Although there are differences the trend is apparent of maximum LIF signal after a residence time of about 20 milliseconds or 180/200 mm downstream of the burner exit, followed by a sharp decay in intensity. The emission of sodium from Individual particles can be clearly seen, each pixel being about 400 microns square. The data is consistent with the average diagram, Figure 5, although the maximum intensity is at least twice the average, reflecting differences in particle concentration in each PLIF image.

The fall off in intensity of the signal after the peak in the average curve at 180 mm downstream of the burner (20 milliseconds) could possibly be attributed to a number of effects. To describe this we need to follow the processes and time scales occurring in the coal particles as they pass through the furnace:

- Initially the coal heats up, devolatilise, rapidly burns out the volatiles by ~ 70 mm (8 milliseconds)
- This is then followed by a period of char combustion, which can be readily observed via streak photographs (used to determine particle velocity), where the coal particles rapidly heat up to the gas temperature and can clearly be seen to be glowing.
- At about 120 mm or 14 milliseconds the intensity of the LIF signal starts to rapidly increase as sodium is volatilised from the coal ash, reaching maximum intensity after 180 mm and 20 milliseconds residence time. This will be affected by non-equilibrium chemistry and especially the presence of CO and hydrogen radicals
- During this time the furnace temperature has been extremely uniform around the 1400°C level, Figure 6, but now starts to fall off
- Chemical equilibrium calculations show that sodium atoms rapidly disappear below 1400°C, with the formation of NaOH and NaCl (if chloride ions are present) and this correlates very well with the drop in temperature in the furnace, Figure 6; this also correlates with increasing oxygen entrainment into the central region of the furnace. Helbe et al measured NaCl concentrations in pulverised coal flames for a number of coals, but carried out detailed equilibrium chemistry calculations involving a range of different sodium compounds to calibrate their measurements. Figure 8 shows their chemical equilibrium calculations for a

Loy Yang Australian coal containing 0.35% sodium, 0.28% sulphur with 20% excess air. It is clear that due to the low partial pressure little sodium exists below 1400°C in the atomic state, the sodium rapidly reacting to form a number of other compounds such as NaCl, Na₂SO₄, NaOH, Na₂O. These are not detected by the PLIF system used here

- The effect of non-equilibrium chemistry is known to be important, especially in reducing atmospheres, which can enhance the concentrations of sodium atoms via reducing reactions. Helbe et al also made some useful calculations on non equilibrium effects, showing timescales for rapid changes in concentration of order 1 to 2 milliseconds between 1200K and 2000K
- Concentrations of sodium are also very small in this coal and thus there are also depletion effects as well

Discussions and Conclusions

This paper has shown new work illustrating the evolution of sodium atoms from a pulverised coal particles burning in a small flat flame burner and furnace at temperature levels representative of those found in large pulverised coal furnaces and boilers using low NO_x burners. Sieved coal was used with 100% < 67 microns and mean diameter of around 50 microns in order to minimize the variation in burning and devolatilisation behaviour. Particulate velocities were measured by streak photography of the char burning in the devolatilised coal particles. PLIF imaging of the essentially one dimensional flame, using a polarisation filter to reduce as much as possible mie scattering clearly showed the presence of sodium emission from the coal particles. This was confirmed by detuning the laser from the PLIF frequency.

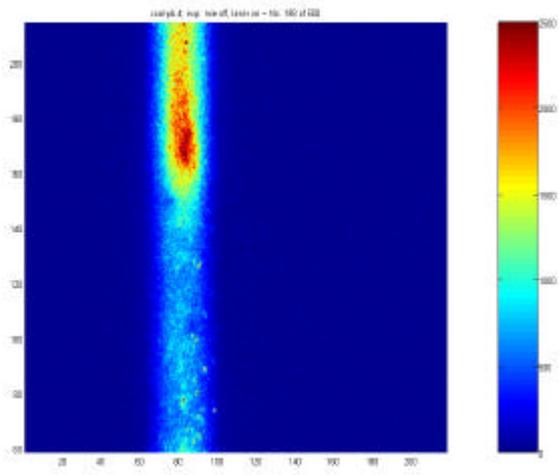
Analysis of the data so obtained showed that the sodium emission reached a maximum after about 20 milliseconds on average, devolatilisation and combustion of devolatilisation products was finished after 9 milliseconds. The emission of sodium is thus for this coal a function of the residence time at the 1400°C level, which cause emission of sodium to reach its peak at 20 milliseconds, thereafter the drop in temperature has a very significant effect, causing a rapid drop in measured sodium atom concentration. Other effects include non equilibrium chemistry and depletion effects in the ash in the coal particles.

In terms of boiler fouling it is clear that for sodium at least it is desirable to keep the residence time of coal particles in the high temperature region for as short a time as possible to avoid minimize formation of sodium atoms and associated chemical reactions

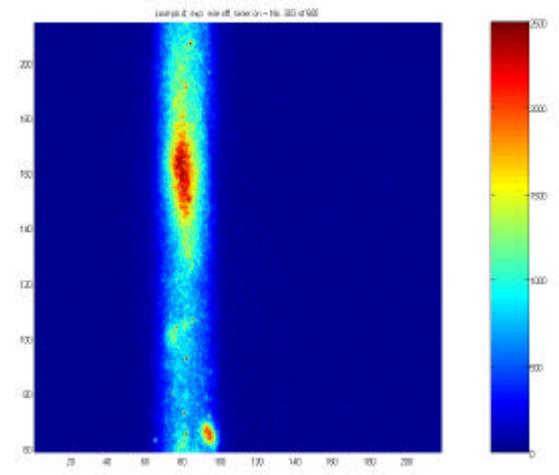
For the future more data is required for a wide range of different coals, with different time/temperature profiles and atmospheres. The technique is quite robust and also needs to be extended to cover the downstream region in more detail. A wider range of volatilised atoms are also required, relevant to deposition and fouling problems in boilers. This should include, copper calcium, aluminium, and phosphorus and for many co-firing applications heavy metals as appropriate

Obviously to accompany this experimental work detailed chemical equilibrium/non-equilibrium analysis needs to be undertaken to describe the processes occurring at these elevated temperatures.

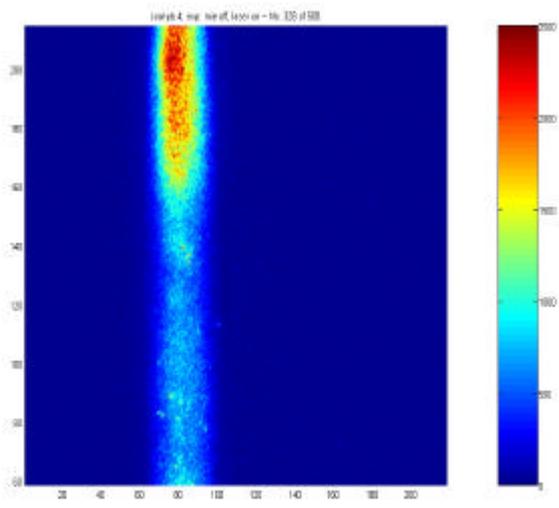
Finally this should lead to new models for deposition and slagging in boilers and furnace which can be incorporated into CFD or other codes.



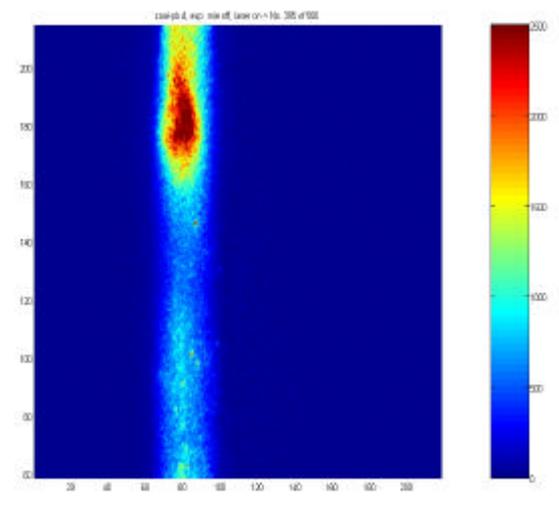
a)



b)

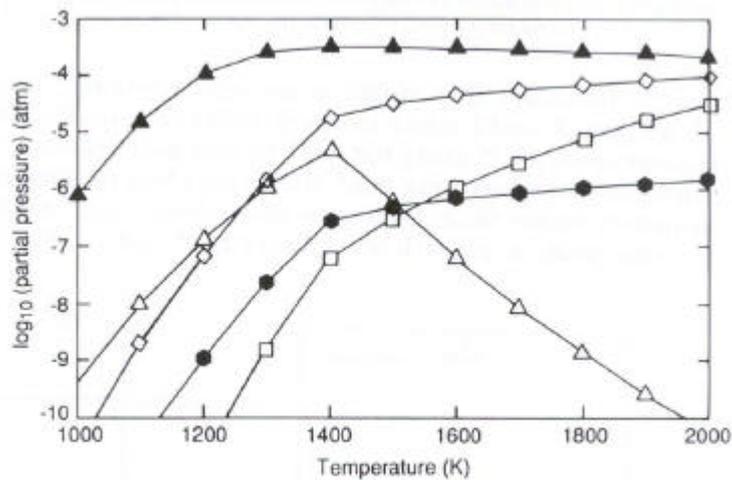


c)



d)

Figure 7 Instantaneous Images for the 500 PLIF Images



Equilibrium Calculations Showing the Major Gas Phase Species for Post-combustion Gases Generated During Oxidation of Loy Yang. (□) Na, (▲) NaCl, (◇) NaOH, (Δ) Na₂SO₄, (●) NaO₂:

Figure 8: Equilibrium calculations for 20% excess air Combustion of Loy Yang Coal (Helble et al).

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References

- Eckbreth (1996): Laser Diagnostics for Combustion Temperature and Species, Gordon Branch Science Publications South Australia.
- Helbe, J.J., Srinivasachar, S and Boni, A.A., (1992), Measurements and Modeling of Vapor-Phase Sodium Chloride formed during Pulverised Coal Combustion, Combustion Science and Technology, Vol 81, p 193-205
- Nathan, G.J., Ashman, P.J., Alwahabi, Z.T., Lucas, O., Meeuwissen, K., (2003): A Comparison of the Spatio-Temporal-Emission of Sodium from Standard and Dewatered Loy Yang Coal using PLIF, Proc 2003 Australian Symposium on Combustion & the 8th Australian Flame Day, Monash University, December 2003