RETROFIT IMPACTS OF OXY-COAL COMBUSTION OF PRB COAL ON DEPOSIT FORMATION AND MERCURY SPECIATION

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Oxy-coal combustion (i.e. combustion with pure oxygen rather than with air) is a viable technology allowing the use of PRB coal to yield a concentrated CO2 stream that can be sequestered underground. The technology uses boiler configurations very similar to those used for conventional air combustion and is therefore suitable for retrofit to existing units. CO2 sequestration technology applied to existing units can have a significant impact on national CO2 emissions. Whereas much pilot scale testing on units up to 30MW has shown that there are few technical impediments to the application of oxy-combustion to boilers that look very like existing boilers, there has hitherto been little corresponding work demonstrating the effects of oxy-combustion on ash deposit formation and fouling of heat transfer surfaces. This report describes results of research completed by the University of Utah on retrofit impacts of oxy-coal combustion of PRB coal on:

1. deposit formation and
2. mercury speciation

Research on deposit formation has:

- Led to the development of a novel temperature controlled deposit probe that allows sampling of deposits under well-defined conditions, and, by separating the initial deposit layer next to the heat transfer surface from the outer deposit layer, it allows growth of the early stages of deposit formation to be investigated.
- Revealed that the initial sticky layer of material deposited on a cooled heat transfer surface consists of ultrafine aerosol particles that are transported to the surface by thermophoresis, rather than by molecular or Brownian diffusion,

- Resulted in an understanding of the relationship between the size segregated composition of the suspended ash aerosol to the composition of both the initial deposit layer as well as the bulk outer deposit layer.
- Determined how ash aerosol and deposits differ between air firing and
    - Oxy-firing using once through CO2 to simulate recycle of cleaned flue gas, and various concentrations of oxygen in the incoming oxidant stream.
    - Oxy-firing using actual recycled CO2 under various flue gas recycle options, with and without particulate removal, with and without water removal, and with and without sulfur dioxide scrubbing.

Research on mercury oxidation has shown that

- Extents of homogeneous mercury oxidation were somewhat higher (in the presence of chlorine or bromine) under oxy-combustion conditions that under air firing conditions.
- Addition of $CaBr_2$ or activated carbon was able to capture up to 95% of mercury from coal combustion, after a baghouse used to collect particulate matter.
- There was little difference between air or oxy-firing in capturing mercury using $CaBr_2$ or activated carbon as a sorbent.

The ash deposition experiments were conducted on a 100kW maximum rated down-fired oxy-fuel combustor (OFC), which is sufficiently small to allow systematic control of inlet gas flow rates and wall temperatures, and yet large enough to simulate the self-sustaining combustion conditions of full scale units, especially in terms of temperatures, coal particle concentrations and mixing. Figure 1 shows a schematic of the combustion rig. Nine pairs of ports are positioned along the vertical section of the OFC for sampling and observation (marked as P1-P9 in Figure 1). In this work deposit samples were obtained at Port 5, Port 6 and Port 7. Although the flame in the ignition zone is a pulverized coal turbulent diffusion flame, the flow laminarizes downstream (Reynolds Number is 743 for the OXY50 case and 1153 for the air case), so that by the time the flow reaches the deposit probe positions at Ports 5, 6 and 7, it is quite laminar with vertical streamlines and few turbulent eddies.

Table 1 summarizes the operating conditions for which experimental data were obtained.

Table 1. Experimental cases abbreviation and description

Case abbreviation	Description
Air	air combustion
OXY50 Once	oxy-coal combustion with 50% inlet O_2 and once through CO_2
OXY27 Once	oxy-coal combustion with 27% inlet O_2 and once through CO_2
OXY50-Ash	oxy-coal combustion with 50% inlet O_2 and RFG after bag house
OXY27-Ash	oxy-coal combustion with 27% inlet O_2 and RFG after bag house
OXY50-Ash-H_2O	oxy-coal combustion with 50% inlet O_2 and RFG after condenser
OXY27-Ash-H_2O	oxy-coal combustion with 27% inlet O_2 and RFG after condenser
OXY50-Ash-H_2O-S	oxy-coal combustion with 50% inlet O_2 and RFG after scrubber
OXY27-Ash-H_2O-S	oxy-coal combustion with 27% inlet O_2 and RFG after scrubber
OXY27-Dirty	oxy-coal combustion with 27% inlet O_2 and dirty RFG

Table 1 shows that this investigation focused on

- Effects of changes in the *amount* of recycled flue gas, as exemplified by the variation of inlet O2 content, and
- Effects of changes in the *composition* (or degree of cleanup) of the recycled flue gas

It should be noted that in this work, the focus is on deposition *chemistry* differences, rather than on deposition *rate* differences. The latter are clearly combustor and flow dependent and will be addressed in future work through a combination of experimentation and simulation. It is recognized that in these experiments the residence time scales differ somewhat from those of full scale units. However, particle concentrations and other attributes are closer to full scale units than those same quantities would be for bench scale drop tube furnaces, while the ability to conduct systematic studies and control experimental variables is still retained..

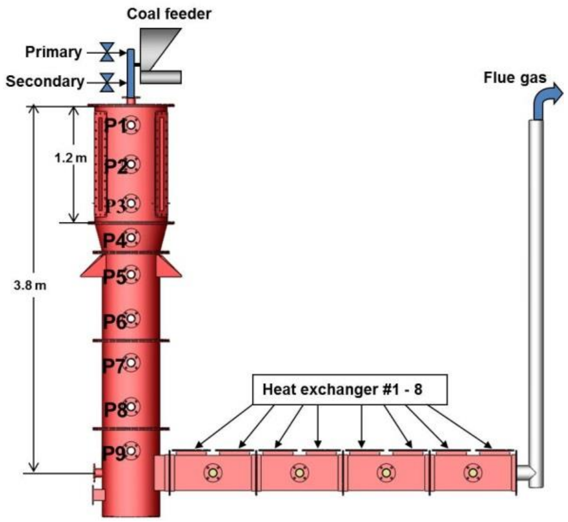

Figure 1. Structure of oxy-fuel combustor (OFC)

In the research presented here, a novel wall temperature controlled deposit probe is described, and it is shown how, together with a prototype combustion system, it can be used to collect and isolate the “inside” and “outside” ash deposits for analysis and deposit mechanism development. The deposit probe is then tested and utilized to compare both “inside” and “outside” deposits for a range of oxy-fired and air-fired combustion conditions, as described on Table 1.

The ash deposition measurements were accompanied by an extensive characterization of the ash aerosol that was responsible for the deposits. To obtain ash aerosol information, two groups of instruments were utilized:

1) A Berner Low Pressure Impactor (BLPI), that allowed the size segregated collection of aerosol particles to be analyzed, and

2) a combination of particle sizers (Scanning Mobility Particle Sizer, SMPS combined with an Aerosol Particle Sizer, APS). This allowed a finely resolved particle size distribution for particles from 0.014μm through 20 μm to be obtained using a combination of electric mobility and light scattering techniques.

The BLPI consisted of 11 stages, with corresponding 50% aerodynamic cutoff diameters of 15.7, 7.33, 3.77, 1.98, 0.973, 0.535, 0.337, 0.168, 0.0926, 0.0636, and 0.0324 µm. Cellulose acetate membranes were used to collect ash aerosol samples for subsequent composition and morphology analyses. Aluminum filters coated with Apiezon grease were used for PSDs. A high-quality Mettler Toledo balance with a precision of 0.1 μg was used to obtain the aluminum filters pre-and post-mass difference.

The SMPS produces a PSD in the size ranges of 0.0143 µm to 0.6732 µm and is combined with an APS that is good for particle sizes in the size ranges of 0.532 µm to 20 µm. The BLPI sampling system includes a water-cooled, nitrogen-quenched isokinetic sampling probe, a cyclone, a BLPI, a vacuum pump, a nitrogen gas cylinder, and a flow meter. The SMPS/APS sampling system includes the same water-cooled, nitrogen-quenched isokinetic sampling probe, a nitrogen gas cylinder, a flow meter, clean compressed air, an orifice, SMPS, APS, and a dilution manifold. The SMPS/APS sampling system, with a total dilution ratio of about 200 to

400 to 1, uses two-stage dilutions to prevent further interactions between particles. Care was taken to sample isokinetically for all conditions, by adjusting the dilution nitrogen flow at the probe tip. This ash aerosol collection system allowed the effects of firing conditions on ultra-fine, fine and coarse ash particle formation to be explored, simultaneously with collection of deposits under well-defined conditions. This work is the first work of its kind where this extent of analysis of the ash aerosol is available together with extensive analysis of the deposits formed.

Table 2 summarizes the ash deposit and aerosol analysis and collection methods employed. In addition effects of variations of deposit probe temperature (from a base of 923K), and position (from a base Port Number of 6) were also explored. Particle analysis was by Scanning Electron Microscopy with Electron Dispersion Spectroscopy (SEM-EDS) or by Computer Controlled Scanning Electron Microscopy with EDS, as shown on Table 2.

Table 2. Ash collection/sampling methods

	Deposition		**Ash Aerosol**		**Bulk Ash**
	Fouling	**Slagging**	**<0.6 µm**	**<16 µm**	
Port Number	6	4	9	9	9
Probe surface temperature (K)	923	-	-	-	-
Residence Time	0.5h, 1h (inside, outside, vertical, side)	4h	135s, 20s	30 – 60 min	30 min
Instrument	Deposition Probe	Slagging Probe	SMPS, APS	BLPI	PC filter
Analysis method	CCSEM, SEM-EDS, weight measure (deposition rate)	CCSEM, SEM-EDS, weight measure (deposition rate)	-	SEM-EDS	-

Data, and figures showing data plots resulting from the experiments performed are presented in the Final Technical Report. Here we present only a summary of the salient results obtained

The deposit/ash aerosol work has led to the following results:

1. A new deposit probe was shown to allow temporal resolution of the formation of the initial layer alone, as well as that of the outer layer. The composition of these layers is very different, and it is erroneous to lump them both together as bulk deposits, if determination of deposit formation mechanisms is desired.
2. The composition of the initial layer depends on the composition of the ultra-fine aerosol. Both depend on the extent of flue gas recycle during oxy-firing, and, presumably, on the peak flame temperature.
3. The inside layer deposition *rate* is proportional to the temperature difference between the flue gas and the deposit surface. This suggests that the primary mechanism of deposition for the inside layer is by thermo-phoresis, and not by Brownian or molecular diffusion.
4. The fouling deposition *rate* is also a function of particle concentration in the flue gas.
5. Air firing led to a higher concentration of sodium in the ultra-fine fume than oxy-firing with 50% O2 in the inlet, and also to a higher concentration of sodium in the inside (initial) deposit layer, but not in the bulk. This is probably because sodium vapor is scavenged more easily by silicates and alumino-silicates at higher temperatures.
6. Although there is a significant difference in the sodium composition of the ultra-fine aerosol formed during oxy-coal combustion with 27% inlet O2 and that with 50% inlet O2, this difference is not reflected in the inside fouling deposits.
7. Air firing led to a lower concentration of silicon in the ultra-fine fume than oxy-firing with 50% O2 in the inlet, and also to a lower concentration of silicon in the inside (initial) deposit layer, but not in the bulk deposits. One would expect that higher flame temperatures lead to increased silicon vaporization (possibly as the suboxide) and to a

shift of the silicon distribution to the smaller particles. The increased surface area allows increased sodium vapor capture on the particles greater than those in the fume.

8. Ash aerosol size distributions measured by electric mobility and light scattering methods (SMPS + APS) agreed well with gravimetric metric measurements using the Berner Low Pressure Impactor, especially for particles greater than 1µ. Although the small amounts of ultra-fine particles, weighed gravimetrically may have been influenced by adsorption of moisture during handling, the general agreement between these methods is encouraging, since each employs very different measurement principles.
9. Surprisingly, the composition of the recycled flue gas, as determined by the extent cleanup in the flue gas recycle loop, did not create a first order effect on the size segregated aerosol composition or the composition of either the inside or outside deposits. However, sulfur scrubbing using a wet calcium oxide spray appeared to allow some entrainment of the calcium sulfate leading to a surprising increase of the sulfur content of the inside deposits for that condition.
10. Interestingly, the sulfur content of the *slagging* deposits, obtained from uncooled ceramic probes inserted into the upper furnace, above the controlled wall temperature controlled fouling deposit probes, showed a strong effect of flue gas recycle composition.

Mercury oxidation and capture by halogens and activated carbon, under air-fired and oxygen-fired conditions, were studied in two reactors: a pulverized PRB coal-fired, 125 kW unit (Oxy-Fuel Combustor (OFC)) equipped with a baghouse and a quartz-lined, 300 W, methane-fired reactor. Both were operated at 27% O_2 in CO_2 for oxygen firing.

Mercury capture in the OFC, before and after the baghouse, was about 40% without additives. The addition of $CaBr_2$ or activated carbon increased mercury capture to about 95% after the baghouse. Capture was about the same for air- and oxy-firing conditions. There was a general increase in mercury removal after the baghouse because of mercury capture in the filter cake.

Gas-phase mercury oxidation was also studied at bench-scale in a laminar, methane-fired, 300 W, quartz-lined reactor. The composition of the flue gas was varied to include chlorine, bromine, SO_2, and NO. Extents of oxidation at chlorine concentrations of 100 to 500 ppmv (as HCl) ranged from 6 to 21% for oxy-firing and from 4 to 15% for air-firing. Oxidation by bromine at concentrations of 10 to 50 ppmv (as HBr) ranged from 43 to 69% for oxygen-firing and from 15 to 46% for air-firing. The addition of NO (below 300 ppmv) had little or no effect on mercury oxidation by chlorine or bromine; and the addition of SO_2 (below 400 ppmv) had no impact on oxidation by chlorine. A possible explanation for higher oxidation under oxy-firing conditions is that CO_2 molecules are more effective than N_2 at removing energy from the HgCl and HgBr transition-state complexes. Extents of oxidation in the coal-fired reactor were insensitive to firing conditions because the dominant mode of oxidation in that particle-laden environment was heterogeneous.