MICROWAVE CARBON BURNOUT (MCB)

GAS BYPRODUCTS AND DEPORTMENT OF SPECIFIC METALLIC ELEMENTS

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EXECUTIVE SUMMARY

The Microwave Carbon Burnout (MCB) process reduces CCP fly ash LOI to any prescribed limit and simultaneously eliminates adsorbed ammonia products. The MCB process generates CO_2 as its principal gas byproduct, does not require auxiliary fuel and has no effect on carryover of resident trace heavy metals which are characteristic of the coal fuel.

Results of extensive pilot testing are reported involving CCP ashes from several US and Canadian sites.

1.0 Process Description

Coal Combustion Product (CCP) fly ash contains residual unburned carbon as a result of (i) imperfect primary combusters and, more significantly, (ii) reduced burner temperature arising from NO_x emission restrictions. This carbon content is characterized by the Loss On Ignition (LOI) and, numerically, the LOI is taken as approximately 1% less than the carbon content.

LOI is measured as the percent mass loss when an ash sample is completely combusted under oxidizing conditions typically at 750ºC. The carbon content is inferred as being approximately 1% greater than this value.

CCP fly ash is a microwave receptor, due primarily to the very high receptivity of elemental carbon even when present in relatively small concentration (few percent down to fractional percent). The MCB process uses microwave energy to provide the combustion energy needed to oxidize the carbon to any prescribed level.

Where the carbon concentration is sufficient to support autothermal operation (approximately 7%-9% depending on reactor design), the microwaves provide startup and throttle energy; in this operating mode, temperature control is by means of oxygen and microwave control. Where the carbon content is below autothermal levels, microwaves provide makeup combustion energy and the process is throttled by both oxygen and microwave control. In either situation, the process is completely controllable and throttled.

Ammonia compounds (usually a form of ammonium sulfate) may become adsorbed to the fly ash in situations where ammonia injection is used to reduce NO_x flue gas levels. This situation, characterized as ammonia slip, results in the gradual release of ammonia gas from the fly ash as it is landfilled or otherwise used, for example, in cement construction. Although not detrimental to the structural value of the cement product, ammonia is considered to be a worker health hazard in concentrations above approximately 100 ppm.

Ammonium sulfates decompose thermally at temperatures consistent with the burning of carbon; in fact, thermal processes are the only means of reducing these compounds to ammonia (gas) and water (vapor). By feeding the gas stream from the fly ash burnout process into the coal combustion plant flue gas stream (ahead of the scrubber), the regenerated ammonia can be used to displace a portion of the ammonia injection requirement.

The MCB process uses a fluidized bed reactor with atmospheric air as the oxygen source. The reactor is operated in a continuous feed mode using overflow discharge as the primary means of removal of processed ash. Steady state reactor temperature (measured in the bed) is in the range 650°C - 850°C and can be regulated to within less than 5 C°. Product residence time is controlled by means of the input feedrate.

2.0 Experimental Program

EMR has conducted tests on CCP fly ash obtained from several US and Canadian utility operations, with LOI ranging from 4-30%. Four of these operations included ammoniated ash with ammonia concentrations ranging from 3-1194 ppm.

For the test program reported here the MCB process utilized a 12 inch diameter fluidized bed continuous feed reactor operating at up to 2 tpd throughput (Figure 1).

All ash samples are homogenized and subjected to both chemical and mineralogical analysis as reported herein.

Tests are conducted by preheating the resident fluidized bed with microwave energy to approximately 600°C, at which point carbon combustion can commence. Fly ash is introduced into the reactor (within the resident bed material) and the bed temperature is increased to the target level (approximately 850°C) by using adjustments in microwave power and material feedrate.

Continuous on-line measurements are made including:

- temperatures
- all gas flows
- material feed rate
- NO_x, SO_2, CO, O_2
- microwave power

Tests are typically conducted over a continuous, steady-state period of at least 3 hours.

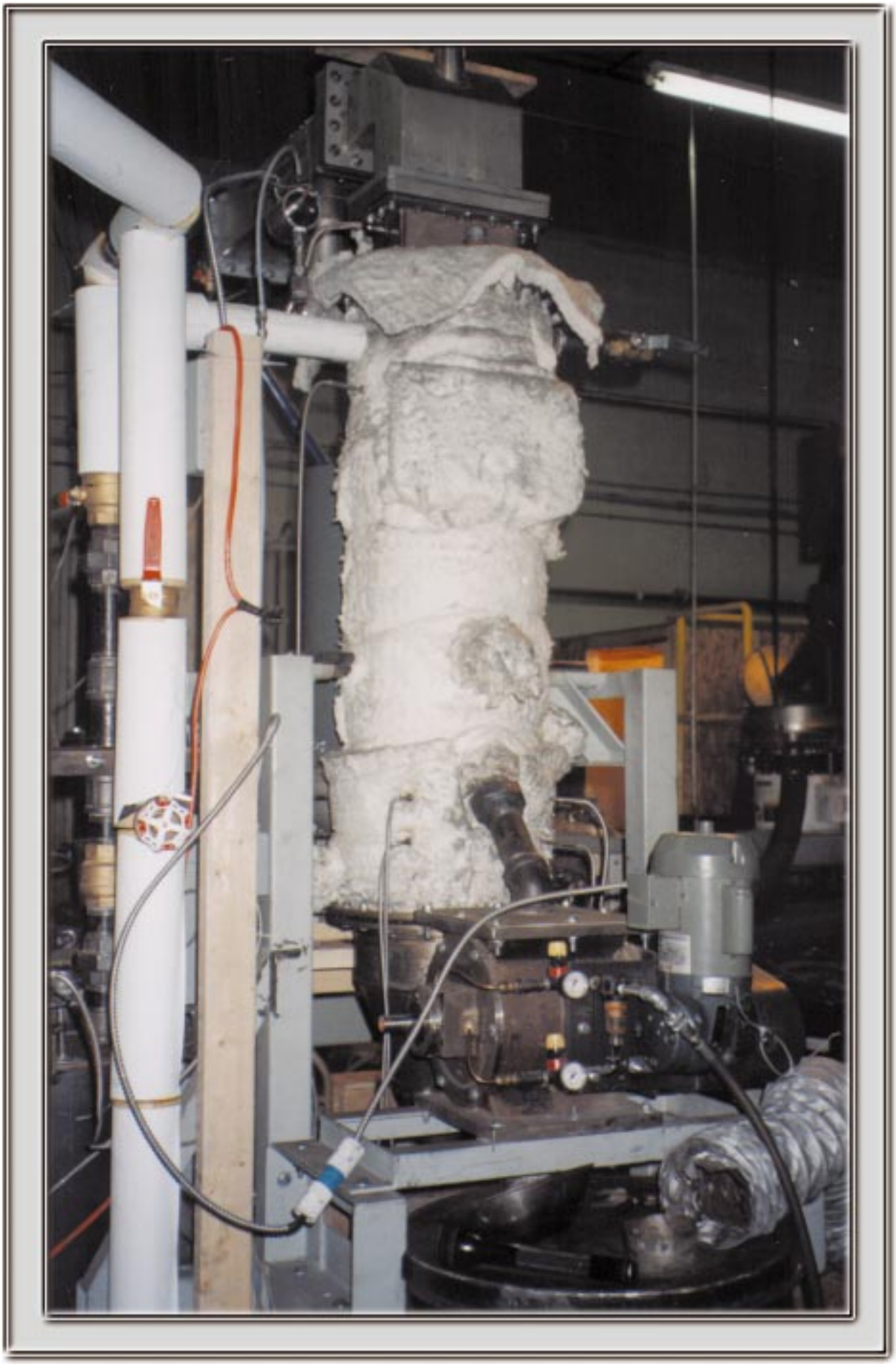

Figure 1 EMR Pilot Test Unit
12 inch Reactor

3.0 Solid Product Analysis

3.1 Loss on Ignition (LOI)

All samples collected for LOI measurement are subjected to a standard (ASTM) oxidizing roast at 750ºC in an electric furnace until mass loss has stabilized. LOI is expressed as the percent mass loss before and after the roast.

EMR's MCB process does not require that the fly ash contain sufficient carbon for autothermal operation; oxidation energy is derived from available carbon combustion as well as from direct microwave input. The MCB process, therefore, is equally effective for any LOI ash. Test samples had LOI ranging from 4% to 30%.

MCB process control is by means of electronic microwave power adjustment; reactor temperature response is nearly immediate. Temperature control in pilot operations has been routinely maintained within 5 C°. Temperature control and reactor residence time are the determining factors for the ash product LOI. Actual product LOI measurement is used to confirm product quality. Product LOI was maintained to ±0.5% regardless of the input LOI.

3.2 Heavy Metals

Material balances have been performed on fly ash subjected to the MCB process. Metals of interest include prinicpally arsenic and mercury. Test data are shown in Table 1 and Table 2.

ARSENIC

Ash samples (before and after MCB) were analysed using both X Ray diffraction (XRD) and ICP Spectrometer to determine the chemical and mineralogical composition.

XRD analysis confirms that naturally occurring arsenic present in the raw (unprocessed) fly ash is not in the form of arsenolite (arsenic trioxide, As_2O_3) or in pyritic (arsenopyrite, FeAsS) form. This is consistent with the coal combustion environment which would have certainly oxidized any pyritic mineralization. If arsenolite were formed in the process of coal combustion it would have readily passed to the atmosphere in the hot flue gas stream.

XRD analysis of the processed ash (post MCB) also confirms the absence of arsenolite and arsenopyrite. Any arsenic present is therefore in a very thermally stable form which remains unaffected by the MCB process. Where incorporated into concrete, these products are permanently prevented from becoming water/air mobile and become permanently stabilized within the concrete matrix.

MERCURY

Mercury is volatilized at temperatures > 357ºC and likely has a vapour pressure below this temperature. The MCB process operates above this temperature and would therefore be expected to volatilize any mercury present. Testing indicates that a large proportion of the mercury present in the fly ash is volatilized, but is then recondensed on the finest, relatively cool particulate that bypasses the cyclone (in the pilot set-up). The proposed design for a commercial MCB unit has the off-gas stream from the fluidized bed reactor being cooled below the volatilization temperature for mercury before passing through a cyclone and baghouse.

Therefore, it is anticipated that during commercial processing the mercury will report back to the combined (calcine, cyclone and baghouse) product ash.

Table 1

ARSENIC BALANCE

Sample No.	1	2	3	4
Total Arsenic In (ppm/gms)	63 / 8.32	77 / 7.45	194 / 24.02	218 / 18.17
Total Arsenic Recovered (ppm/gms)	129 / 13.84	92 / 7.34	273 / 26.66	282 / 19.50
Loss (gms)	-5.52	0.11	-2.64	-1.33
Loss (%)	-66.39%	1.54%	-10.98%	-7.32%

Table 2

MERCURY BALANCE

Product		Hg/ppb	Mass/lb	Mass/g	HgMass/g
Calcine T167		22	0.20	90.72	0.000020
Cyclone T167		23	1.10	498.95	0.000115
Calcine T197		11	0.20	90.72	0.000010
Cyclone T197		1	1.60	725.75	0.000007
Dry Calcine		15	9.50	4309.13	0.000646
Dry Cyclone		2	26.85	12178.97	0.000244
Calcine T392		8	0.65	294.84	0.000024
Cyclone T392		2	0.95	430.91	0.000009
Calcine T419		7	0.20	90.72	0.000006
Cyclone T419		3	1.10	498.95	0.000015
Final Calcine		14	25.70	11657.34	0.001632
Final Cyclone		4	43.60	19776.65	0.000791
Sintered Filters	* See Note	5392	1.15	521.63	0.028126
Reject		8	67.35	30549.48	0.002444
Reactor Calcine -10 mesh		7	21.05	9548.13	0.000668
Reactor Calcine +10 mesh		0		27.50	0.000000
Quenched Calcine		21	3.40	1542.22	0.000324
Quenched Cyclone		4	10.30	4672.01	0.000187
Total Product				97504.62	0.035268
Material In		61		123717.47	0.075468
% Difference				21.19	53.27

* Note : Mercury concentration readings vary from 3700 - 5400 ppb and are beyond the range of accurate instrument calibration.

3.3 Ammonia Compounds

Testing of ammonia concentration in fly ash samples was conducted using the American Public Health Association (APHA) Method 4500-NH3E involving a distillation-titration technique.

By analysis, ammonia compounds (principally ammonium sulfates) are reduced in the MCB process (at approximately 800°C) to form ammonia (gas) and water vapor, both of which are passed in the exhaust gas stream.

Ammoniated ashes from four utility stations were put through the MCB process for LOI reduction. Ammonia concentrations (Table3) were measured in both the input and output ash streams.

Table 3

AMMONIA CONCENTRATION

Ammonia (ppm)		Test	Comments
Feed	Processed		
1194	25	Batch	Scoping
146	112	Batch	Scoping
856	372	Batch	Including pet coke
15	nil	Pilot	
3	nil	Pilot	Including pet coke
8	nil	Pilot	
776	20.0	Pilot	
776	8.3	Pilot	
776	8.2	Pilot	
776	5.7	Pilot	
776	2.6	Pilot	
776	2.9	Pilot	
776	3.3	Pilot	
776	4.7	Pilot	
776	1.7	Pilot	
776	1.4	Pilot	
776	nil	Pilot	
776	nil	Pilot	
776	nil	Pilot	
776	nil	Pilot	
776	4.7	Pilot	
776	2.2	Pilot	
776	2.7	Pilot	
776	3.2	Pilot	
776	5.7	Pilot	
776	4.8	Pilot	
776	3.9	Pilot	
776	4.2	Pilot	
776	nil	Pilot	
776	nil	Pilot	

4.0 Gas Product Analysis

EMR's fluidized bed MCB reactor operates at a bed temperature in the range 750°-850°C. Exhaust gases at the reactor outlet are in the range 800°C; this gas stream passes through one or more cyclonic separators for removal of particulate and the hot gas is then redirected into the generating station gas stream ahead of the scrubbers.

Fluidizing gas for the MCB process is atmospheric air. The reactor is run with approximately 2%-4% excess oxygen (as measured in the exhaust gas stream). Bottled nitrogen gas is held in standby for emergency purging of the reactor or as an auxiliary means of temperature control for very high fuel value ash.

4.1 Carbon Dioxide (CO_2)

The MCB process combusts residual carbon to form CO_2 gas as its principal gaseous product. The stoichiometric rate of production is 3.67 kg CO_2 per kg carbon.

4.2 Nitrous Oxide (NO_x)

MCB operating temperatures are in the range 750°-850° C which are significantly below the threshold (>1300°C) at which the kinetics for thermal NO_x formation become significant.

Continuous (on line) NO_x measurements during tests on several ash samples, including both non-ammoniated and ammoniated ashes, indicate the following:

- zero NO_x produced when the host bed is heated to operating temperature in the absence of fly ash
- NO_x generation commences immediately with (unammoniated) ash feed at temperatures as low as 600°C
- NO_x generation appears to be related to LOI but does not appear to be proportional to the actual amount of carbon which is combusted.
- chemical analysis of unammoniated ash indicates no trace of nitrogen compounds, thus discounting fuel NO_x as the source of NO_x generation.
- a "typical" NO_x generation level for an unammoniated ash, 10.8% LOI, is 200-300 ppm at a feedrate of 0.5-1 lb/min, flowrate 12-15 cfm is approximately 0.4-1.0 lb NO_x per ton ash processed, or approximately 0.2-0.6 lb NO_x per million BTU (Figure 2, Table 4)

Table 4

NO_x Measurements - Pilot Test

Time (Minutes)	NO_x (ppm)	CO (ppm)	% O_2 (Downstream)	Average Temp (°C)	Feed Rate (lb/min)	Flow (CFM)	lb NO produced per ton ash processed	lb NO produced per million Btu
112	278	1000	14.7	683	0.50	14.79	1.30	0.63
119	223	1135	14.1	710	0.50	14.95	1.06	0.51
125	217	980	14.0	728	0.50	14.83	1.02	0.50
133	253	936	12.7	745	0.50	14.85	1.19	0.58
149	238	689	12.4	763	0.50	14.85	1.12	0.54
178	213	510	12.0	797	0.50	15.03	1.02	0.49
189	207	464	11.9	795	0.50	15.06	0.99	0.48
202	272	628	11.0	798	0.50	11.13	0.96	0.47
208	211	412	13.3	812	0.50	15.34	1.03	0.50
216	203	450	12.6	808	0.50	15.04	0.97	0.47
224	265	570	7.7	807	0.75	15.06	0.84	0.41
234	235	526	7.3	799	0.75	15.05	0.75	0.36
246	250	420	6.9	799	0.75	15.05	0.80	0.39
252	280	427	6.1	823	0.75	14.61	0.87	0.42
253	293	446	5.3	826	0.75	15.09	0.93	0.45
260	227	398	6.4	811	0.75	14.65	0.70	0.34
265	178	362	7.1	787	0.75	14.99	0.56	0.27
269	191	380	5.5	775	0.75	15.12	0.61	0.30
274	245	439	4.1	789	1.00	15.10	0.59	0.28
282	238	500	2.9	787	1.00	15.11	0.57	0.28
288	218	449	2.9	784	1.00	15.07	0.52	0.25
304	278	1030	4.7	790	1.00	12.89	0.57	0.28
312	406	2000	26.0	801	1.00	12.86	0.83	0.40
315	299	525	4.0	808	0.75	12.06	0.76	0.37
321	331	732	2.9	807	0.75	12.04	0.84	0.41
323	239	349	6.0	807	0.75	15.42	0.78	0.38
330	190	295	6.8	775	0.75	15.32	0.62	0.30
336	190	294	6.6	783	0.75	15.34	0.62	0.30
346	112	180	13.2	777	0.75	15.29	0.36	0.18
354	219	387	5.8	787	0.75	15.42	0.71	0.35
362	215	397	6.2	782	0.75	15.10	0.69	0.33
367	250	401	5.5	801	0.75	14.73	0.78	0.38

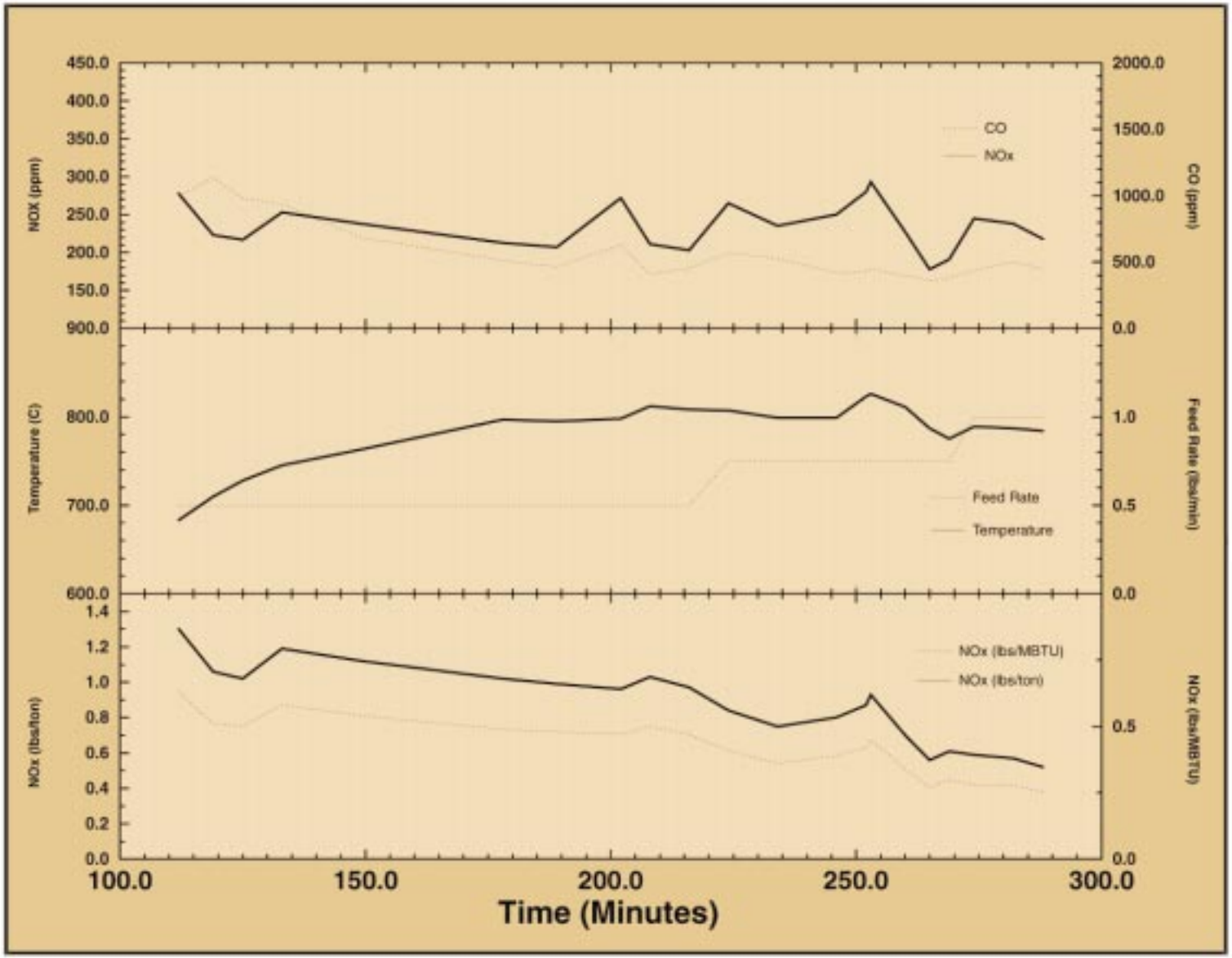

Figure 2 Sample test data record, Pilot operation

5.0 CONCLUSION

The MCB process effectively treats both carbon and ammonia in CCP fly ash. Carbon is oxidized to CO2 and ammonia products are reduced to ammonia gas and we incorprated into the exhaust gas stream.

There is no evidence of movement of arsenic which may be resident in the fly ash in trace amounts from the original coal. No arsenic compounds are formed in the MCB process and non are transferred to the gas stream. Solid compounds, if present, remain in their original form and are reported to the ash product for cementation.

Mercury which is condensed and adsorbed onto the fly ash is revaporized in the MCB process, is incorporated into the gas stream and recondenses/readsorbs onto the fly ash (fines) upon cooling prior to passing to the baghouse filter. Adsorbed solids are incorporated into the finished fly ash product and ultimately are cemented; there are no detectable mercury levels in the cooled exhaust gas stream.