

# SUPER-EQUILIBRIUM CONCENTRATIONS OF CARBON MONOXIDE AND HYDROCARBON IN FUEL GASES AND THEIR RELATIONSHIP WITH VOC AND METALS EMISSIONS

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## INTRODUCTION

Flue gases resulting from the combustion of hydrocarbon fuels in practical systems usually contain levels of carbon monoxide that are significantly above equilibrium values. Typically, for flue gases from a utility plant containing 5% O<sub>2</sub>, the measured level of carbon monoxide is about 300 ppm. The computed equilibrium value is extremely small with 3% O<sub>2</sub> and rises rapidly as the O<sub>2</sub> level is reduced. If combustion took place in the combustion chamber with perfectly-mixed fuel and combustion air, the lower levels of carbon monoxide would result. However, mixing is not perfect because of the formation of coherent structures and large turbulent eddies. These unburned pockets of rich mixtures are caused by incomplete mixing of fuel and air at the near-burner zone, and persist because of the slow subsequent mixing with air. They are responsible for the above equilibrium levels of hydrocarbons, namely the volatile organic compounds (VOC) found in the flue gases.

The super-equilibrium levels of carbon monoxide can also be responsible for corrosion cracking in earlier parts of certain boilers, is related to the presence of unburned hydrocarbons, and can have some influence on the chemistry of the metals emitted. In this paper, values of the super-equilibrium levels of carbon monoxide and VOC's are computed together with their influence on metal emission.

A similar situation can hold for smoke where the concentrations in the rich pocket are above those expected for a uniformly mixed gas. These higher local soot concentrations can coagulate faster and can result in sub-micron particulate matter even in lean mixtures.

## EXPERIMENTAL

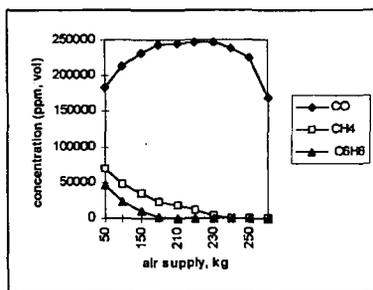
Thermodynamic equilibrium concentrations of major VOCs, certain polycyclic aromatic hydrocarbons (PAHs) and trace element species were determined by means of minimisation of free energy calculations using "Equitherm" (VCH scientific Software, Equitherm version 5.0).<sup>1</sup> The calculations presented here were designed to determine the effect of carbon monoxide levels on species for arsenic, chlorine, cadmium, mercury, nickel, lead and thallium. The system examined uses a sub-stoichiometric basis and calculates the formation of all gaseous, liquid and solid phase species at 1 atm. pressure over a range of temperatures (500 - 1800 K), and amount of air supplied (300, 250, 200 and 150 kg corresponding to between approximately 1/4 to 1/8 of stoichiometric air) and is based on 100 kg of coal. Two coals with very different properties were investigated, Thai coal and Pittsburgh #8 coal, and the analyses of which are given in Table 1.

## RESULTS AND DISCUSSION

Equilibrium predictions of CO concentrations are low compared to CO<sub>2</sub>. However, actual CO concentrations in flue gases are much higher than equilibrium values. These higher CO concentrations could arise from poor mixing in the combustion system, resulting in a drastic decrease in local O<sub>2</sub> concentrations, and consequently increases in CO concentration. Such a situation could be described by the formation of fuel-rich turbulent eddies, which mix, and therefore cool, relatively slowly. Within these fuel rich pockets, reactions of volatile gases, fuel and unburned or partially oxidised species take place in an oxygen deficient atmosphere. Figure 1 describes the change in CO, CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> concentration at 1500 K as the air supply is varied. A rapid increase in CO between 300 and 250 kg air (per 100 kg fuel) is observed. As the mixture becomes richer, benzene and methane also start to increase in concentration,

**Table 1 Summary of characterisation analysis on original coal sample**

	Thal coal		Pittsburgh #8	
	As determined (wt%)	Dry basis (wt%)	As determined (wt%)	Dry basis (wt%)
% ash	25.43	22.54	9.84	9.68
%carbon	56.45	50.04	74.66	73.45
%hydrocarbon	13	11.52	5.2	5.12
%nitrogen	1.69	1.50	1.7	1.67
%oxygen (difference)	3.43	3.04	8.6	8.46
%sulfur	1.98	1.76	2.19	2.15
%moisture	12.81		1.65	
concentration of metal in ppm, wt.				
As	11.28	10.0	3.36	3.31
Cd	0.58	0.5	0.03	0.029
Ni	22.58	20.0	1.70	1.67
Pb	45.12	40.0	1.85	1.82
Tl	1.13	1.0	1.02	1.0
Hg	0.11	0.1	0.12	0.12
Cl	1128.10	1000.0	0.12	0.12
kJ/kg	27110	24030	31960	31440



**Fig 1: Thermodynamic prediction of the equilibrium concentration of CO, CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> at 1500K**

and CO begins to decrease. If calculations are performed at leaner conditions (up to 600 kg air) the CO concentration decreases to very low levels, as do the VOC species.

Figure 2 indicates the concentration profiles with temperature of hydrocarbons at both 150 and 300kg air /100kg coal. Equilibrium conditions are not expected to be attained at lower temperature in the reaction times available.<sup>2</sup> Transient kinetic calculations indicate that the equilibrium concentrations produced at high temperature (i.e. above ~ 1273 K) are reasonable, but that the species are quenched as the rich pockets cool. The window of stability for hydrocarbons is related to O<sub>2</sub> concentration. Concentrations of the larger polyaromatic hydrocarbons (PAH) (C<sub>10</sub>H<sub>8</sub> and C<sub>20</sub>H<sub>12</sub>) are predicted to rise rapidly at lower O<sub>2</sub> concentrations. The increased concentration of PAH and other reduced species results in the increased probability of soot formation and agglomeration, through collision and reaction in the rich turbulent eddies.

Throughout the temperature range studied (500-1800K) the distribution of metals can be followed as shown in Figure 3a and 3b for Pittsburgh coal. The concentration of air affects the overall distribution of the metals between the solid and gas phase. The reduction in air also influences the speciation of the metals causing many of them to be fixed in the solid phase up to a higher temperature. The presence of fuel rich "pockets" in the combustion system appears to be beneficial for many trace metals, because the formation of solid chlorides and sulphides is favoured at higher temperatures for richer pockets. E.g. for 300 kg air, the transformation of cadmium occurs in the temperature range 900 - 1000 K corresponding to the transformation of Cd metal (g) to CdS (s). A slight increase in CdCl<sub>2</sub> effects the distribution of cadmium. For lead, solidification of PbS vapour is expected to be independent of air concentration, and occurs at 700-800 K. The temperature for partitioning of thallium between gas and solid phases is changed slightly by changing the air concentration. In terms

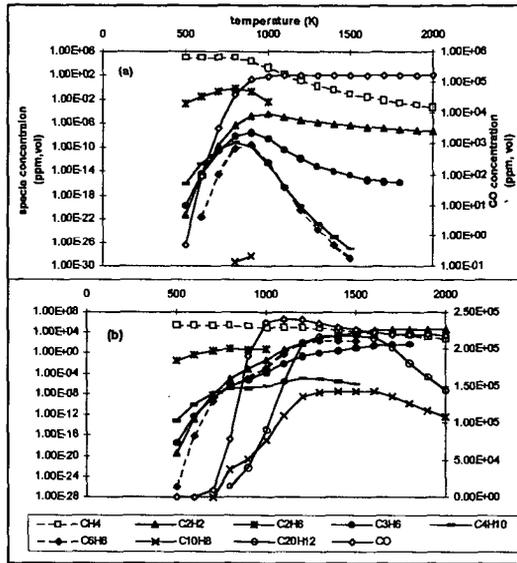


Fig 2: Thermodynamic prediction of equilibrium concentrations of gases for Thai coal: at (a) air 300 kg, and (b) air 150 kg.

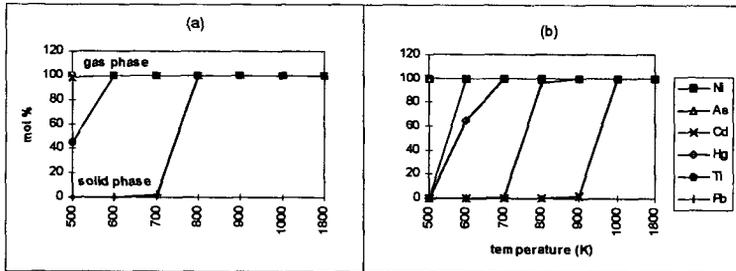


Fig 3: (a) Distribution of metal species in fuel gas and ash for Pittsburgh coal: (a) air 300 kg (b) air 200 kg

of distribution between the phases, Hg remains in the gas phase throughout the temperature range for 300 kg air/100kg fuel (Fig. 3a) predominantly as Hg (metal). At leaner conditions (Fig. 3b) mercury is in the gas phase as HgS (g), which forms a solid phase at low temperatures.

Ni and As are present in the gas phase even at low temperatures regardless of air concentration. Ni is released as Ni(CO)<sub>4</sub> and appears to independent of air concentration. Even at stoichiometric air (or above), nickel carbonyl is predicted to be the most stable nickel species. Figure 4 shows the distribution of metal speciation for nickel. The higher emission for the Thai coal simply reflects the higher concentration of nickel in the original coal.

Arsenic on the other hand is very sensitive to the air concentration, as shown in Figure 5. At 350 kg air, the arsenic is predominantly AsO(g) over the entire temperature range. However at 300 kg air, higher temperature favours the decomposition of AsO(g) and the formation of the highly toxic hydride, arsene (AsH<sub>3</sub>).

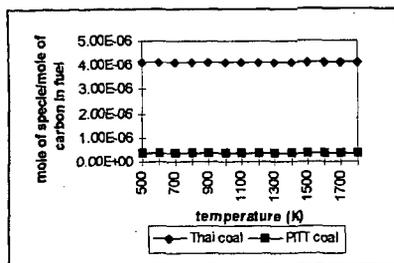


Fig 4: Equilibrium concentration of Ni(CO)<sub>4</sub> for Thai coal and Pittsburg coal with 300kg air/100kg coal

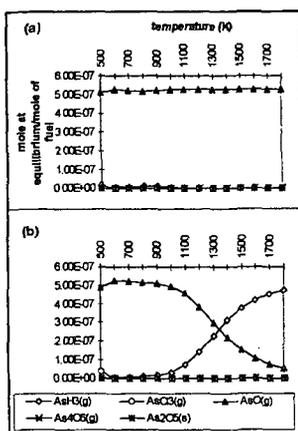


Fig 5: Equilibrium distribution of Arsenic species at 350 (a) and 300 (b) kg of air for Pittsburgh #8 coal.

## CONCLUSIONS

One route to the emission of VOC and PAH from combustion processes is via the formation of fuel-rich turbulent eddies in the flame. The local gaseous environment in these eddies favours the formation of super-equilibrium concentrations of all organic species. The concentration of CO may be used as a marker to calculate emissions of organic species, since a direct correlation is observed, although the nature of the fuel also influences the relative concentrations.

Trace metals, present in the fuel-rich "pockets", are predicted to change their speciation behaviour, compared to a fuel-lean situation. In some cases the thermodynamics acts in favour of decreasing the flue gas emission factor of the metal in question (e.g. thallium). However, the predictions for the influence on the emission of certain metal species (e.g. nickel and arsenic) is of concern. Possible routes to nickel carbonyl and arsene (AsH<sub>3</sub>) are apparent.

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## REFERENCES

1. H.K.Chagger, J.M.Jones, M.Pourkashanian and A.Williams; Fuel, 1997, 76, 9, 864.
2. Barin, I., Thermochemical Data of Pure substances, 2<sup>nd</sup> edn. VCH, Weinheim, 1992.