

# EMISSION OF TRACE ELEMENTS DURING COAL COMBUSTION IN AIR VERSUS O<sub>2</sub>/CO<sub>2</sub> MIXTURES

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Electricity generation from conventional coal firing in air is a major source for the emissions of heavy metals worldwide. In Australia, it contributes to ~31% of the total antimony (Sb), ~42% of the total cadmium (Cd), 38% of the total cobalt (Co), 43% of the total mercury (Hg) and 19% of the total chromium (Cr). Wood burning and waste materials incineration also contribute to a large fraction of hazardous metals including arsenic (As), lead (Pb) and zinc (Zn). These metals are mostly emitted as fine/ultrafine particulates with an aerodynamic size down to 0.01  $\mu\text{m}$ , which are of great concern from a public health perspective. The inhalable ultrafine particles are difficult to capture and transport over long distances in air.

Emission of heavy metals could be substantially influenced with shifting coal combustion from conventional air-firing to oxy-firing. For oxy-firing of coal in O<sub>2</sub>/CO<sub>2</sub> mixture, apart from the accumulation of the impurities including SO<sub>2</sub>, HCl, steam and dust in flue gas, the distinct properties of CO<sub>2</sub> also play an important role in the partitioning of inorganic elements, which has been greatly underestimated or overlooked. For an O<sub>2</sub> fraction of 27~30% in CO<sub>2</sub> to match volatile flame and char temperatures in air (Buhre 2005), a number of issues are still greatly altered when compared with in air: char reactivity, structure and local gas environment (Rathnam 2009); diffusivity of inorganic vapours through char pores and CO<sub>2</sub> boundary layer (Molina and Shaddix 2007); and coagulation propensity of primary nuclei in flue gas.

Char properties can be changed due to high O<sub>2</sub> content and potential char-CO<sub>2</sub> gasification during oxy-firing, which in turn result in distinct char structure and formation of extra reducing gases on char surface to promote the vaporization of heavy

metals and the melting of refractory minerals. For instance, pyrite converts and melts differently in the reducing and oxidizing atmospheres (McLennan 2000), which accordingly influences the diffusion of the pyrite-bound As, *i.e.* arsenopyrite ( $\text{As}_2\text{S}_3\text{-FeS}_2$ ), through the pyrite melt and the diffusion of gaseous As through char pore. The gaseous As may even diffuse differently through the  $\text{CO}_2$  boundary layer on char surface, since a variety of properties such as density and viscosity for  $\text{CO}_2$  differ from  $\text{N}_2$ . The diffusivity of  $\text{CH}_4$  in  $\text{CO}_2$  has been confirmed to be around 20% less than in  $\text{N}_2$  (Molina and Shaddix 2007). All these factors will eventually lead to distinguished vaporization rates for heavy metals in  $\text{O}_2/\text{CO}_2$  mixture.

The emission behavior of Cr in drop-tube furnace and its partitioning between coarse ( $>5.0 \mu\text{m}$ ) and fine ash particles in figure 1 evidenced the importance of bulk gas composition on the emission of heavy metals. As can be seen, compared to case 1 for air, the retentation extent of Cr in coarse ash fraction is greatly reduced with bulk gas shifting to 27%  $\text{O}_2$  in  $\text{CO}_2$  and the addition of steam ( $\text{H}_2\text{O}$ ), HCl and  $\text{SO}_2$  in bulk gas. Apparently, the Cr vaporisation extent is increased during oxy-fuel combustion of Victorian brown coal. Characterisation of the chemical forms of Cr ( $\text{Cr}^{3+}$  versus  $\text{Cr}^{6+}$ ) by X-ray adsorption Near-Edge Spectroscopy (XANES) has also been conducted, which will be further reported to elucidate the behavior of Cr during coal combustion in air versus  $\text{O}_2/\text{CO}_2$ .

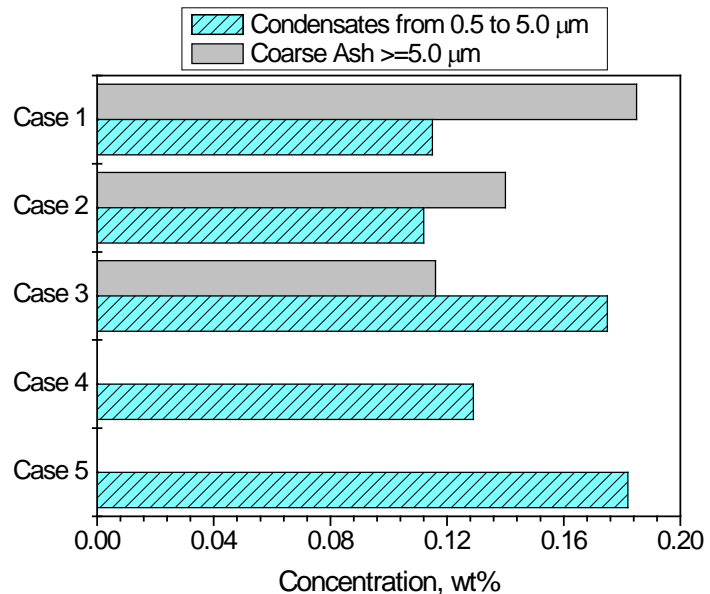


Figure 1 Partitioning of Cr in Victorian brown coal ash generated during combustion at  $1000^\circ\text{C}$  in a variety of bulk gases. Case 1 is air, case 2 is 27%  $\text{O}_2$  in  $\text{CO}_2$ , case 3 is 27%  $\text{O}_2$  and 20%  $\text{H}_2\text{O}$  in  $\text{CO}_2$ , case 4 is the bulk gas of case 3 added with 250 ppm HCl, and case 5 is the bulk gas of case 4 added with 250 ppm HCl and 500 ppm  $\text{SO}_2$ .

## REFERENCES

- Buhre BJP, Elliott LK, Sheng CD, Gupta RP, Wall TF, *Prog. Energy Combust. Sci.*, 2005, 31: 283-307.
- Rathnam RK, Elliott LK, Wall TF, Liu Y, Moghtaderi B, *Fuel Process. Technol.* 2009, 90: 797-802.
- Molina A, and Shaddix CR, *Proc. Combust. Inst.*, 2007, 31: 1905-1912.
- McLennan AR, Bryant GW, Stanmore BR, and Wall TF, *Energy Fuels* 2000, 14: 150-159.