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CFD Modelling of Mercury Behaviour in Air-coal and Oxy-coal Combustion Systems

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Abstract:

In this study, a mechanism for mercury chlorination in flue gases and fly ash particles resulting from the combustion of pulverised coal is presented. A reduced gas-phase reaction mechanism is combined with mercury heterogeneous oxidation on the fly ash particles. The mechanism is used in an advanced CFD model of a pilot-scale test facility and is validated by comparison to available experimental data for air-coal combustion conditions. The model is then used to simulate mercury speciation under oxy-coal combustion conditions. This approach aims to provide an improved prediction of mercury speciation from coal-fired power plants and to elucidate the changes to mercury speciation encountered during oxy-coal combustion.

Keywords: Oxy-coal combustion, mercury speciation, CFD modelling

1. Introduction

The behaviour of mercury under oxy-coal combustion conditions is of interest due to its formation of amalgams with the aluminium used in the downstream cryogenic separation and compression units of the flue gas. Interactions between mercury and other flue gas species are complicated and factors including coal composition, combustion conditions, plant configuration, and temperature-time history from combustion zone to stack can affect mercury speciation. Mercury is vaporized from coal during combustion and released in its elemental form (Hg^0). As the temperature drops in the post-combustion zone of the flue gas line, Hg^0 may undergo a number of transformations. A fraction of mercury may be transformed to an oxidised form (Hg^{2+}) in the gas phase while the remaining of Hg^0 may be oxidised heterogeneously on the fly ash or metal surfaces encountered in the post combustion zone with HgCl_2 believed to be the predominant oxidised form present in the gas-phase. Hg^0 and Hg^{2+} may also be adsorbed onto the surface of the fly-ash or carbon in ash to form particulate bound mercury (Hg^p). Hg^{2+} can be readily removed by wet flue-gas-desulphurisation (FGD) systems due to its high water solubility. The low water solubility of Hg^0 makes it more difficult to capture and therefore it tends to pass through FGD systems. Hg^p is easily separable by fabric filters, electrostatic precipitators and separation cyclones.

Under oxy-coal combustion operation with recycled flue gas (RFG), a number of changes occur to the conditions in the post combustion zone which can potentially impact mercury transformation. Due to the recycle and omission of nitrogen from the system, the concentrations of many of the minor species are elevated. Furthermore, an increase in chlorination of the active sites on the surface of unburned carbon (UBC) could potentially lead to an increase in chemisorption of Hg^0 because halogen loadings on carbon sorbents are believed to enhance the formation of Hg^p . As far as we are aware, there are no detailed measurements of mercury transformation under oxy-coal

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combustion with RFG reported in the literature and the impact of oxy-coal combustion conditions on mercury speciation is still uncertain.

This paper describes the development of a model for the prediction of mercury transformation under air-coal and oxy-coal combustion conditions. A previously developed gas-phase kinetic mechanism for mercury oxidation [1,2] is coupled to heterogeneous processes using computational fluid dynamics (CFD) techniques. The heterogeneous model is based on an assessment of previously proposed mechanisms in the literature and uses data obtained under air-firing mode for model parameter optimization. The model is then simulated under oxy-coal conditions and the results are analysed to assess the impacts on the behaviour of the mercury and its partitioning between various forms (Hg^0 , Hg^{2+} and Hg^{P}).

2. Experimental data

Measurements from a slipstream reactor reported by Cao et al. [3,4] have been used in this study. In the pilot-scale reactor, mercury speciation was monitored at the inlet, middle and outlet of the reactor by means of a semi-continuous emission monitoring system which was confirmed by the Ontario hydro method (ASTM6784-02) for each of the sampling ports. The flue gas from the economizer (~ 300 - 350 °C) is fed to the reactor and insulations ensure a temperature drop of no more than 20 °C along the reactor length. The residence time in the reactor is ~ 1 s. There is no particulate separation unit before the slipstream reactor hence mercury speciation occurs in the presence of fly ash. In order to avoid the deposition of fly ash, a blower is installed at the outlet of the reactor. Downstream of the reactor, hoppers were used to collect fly ash and the samples were analysed for Hg^{P} .

3. Computational approach

A bituminous coal was combusted in air during these tests and its analysis along with the reactor inlet major species flue gas composition used for air-coal and oxy-coal combustion simulations are given in Table 1.

Table 1: Coal analysis and flue gas compositions

Coal analysis (Dry, %)							Flue gas composition (Mol fraction at 623 K, %)						
C	H	O	N	Cl	Hg	Ash	CO ₂	N ₂	O ₂	H ₂ O	HCl	Hg	
72.9	5.0	10.0	1.0	1270 (ppm)	0.1 (ppm)	6.0	14.8	75.4	2.8	6.7	100-600 (ppm)	0.9 (ppb)	Air
							87.2	0.1	2.6	9.9	100-600 (ppm)	0.9 (ppb)	Oxy

Note that the inlet gas composition for the oxy-coal combustion case (which is used for simulation purposes only) is calculated kinetically by consideration of typical time-temperature histories of flue gases and for a once-through combustion in a medium of 30/70 mix of O₂ and CO₂. The meshing software Gambit has been used to generate the reactor geometry and the computational grids. A two-dimensional grid with approximately 21,000 fine rectangular cells has been employed. The numerical modelling is carried out by utilizing the commercial CFD code, ANSYS Fluent v. 12.1. The fluid flow prediction is performed by using the SIMPLE algorithm to handle the velocity-pressure coupling and the turbulence is modelled with standard k - ϵ with default parameters. A linear temperature drop 20°C is imposed on the reactor wall and the flue gas from 632 K (~ 350 °C) at the inlet, therefore no effort has been made to solve the energy transport equation. Transport equations for the gas phase are solved using an Eulerian approach and particles are tracked in a Lagrangian manner across the calculated flow field. A second order upwind scheme is used to solve the continuity, momentum and species transport equations. The convergence criteria are set with residuals for the continuity and momentum equations at less than 10⁻⁴ and scalar equations less than 10⁻⁷.

A Rosin-Rammler size distribution is defined for the fly ash particles on the basis of an average size of 25 μm and that over 65% of the particles are smaller than 10 μm . A measured loss on ignition (LOI) of approximately 2.57 % and initial mercury content on the fly ash particles (at the reactor inlet) of 0.1 ppm is assumed. Homogeneous chemical reactions are defined by means of a CHEMKIN input file whereas heterogeneous reactions are specified with user defined functions. The gas-phase Hg-Cl mechanism is an updated and reduced version of our earlier mechanism given in [1,2] consisting of 20 species in 51 reactions. The gas-phase mechanism is coupled to a

heterogeneous mechanism of four surface species and two globalised gas-solid reactions in order to describe the reaction chemistry during the calculations. A stiff chemistry solver is used with absolute and relative residual errors being set to 10^{-20} during the numerical solutions.

For heterogeneous oxidation of mercury on the particle, a Langmuir-Hinshelwood type mechanism is assumed for modelling the adsorption, desorption and reaction processes of Hg^0 and HgCl_2 on the fly ash. Rate parameters are estimated by fitting the measured Langmuir rate parameters using the procedure reported by Karatza et al [5,6] in an Arrhenius form equation. Karatza et al. measured HgCl_2 adsorption and desorption rates on a variety of fly ash and activated carbon at a temperature range of 350-400 K. In a similar study, Serre et al. [7] calculated Langmuir parameters for Hg^0 adsorption on the fly ash and selected activated carbons in the temperature range of 363-450 K. In this procedure, the adsorption-desorption equilibrium constant is found through a non-linear regression of the Langmuir parameters. For both Hg^0 and HgCl_2 , rate parameters referring to maximum adsorption are considered.

4. Results and discussion

4.1. Air-coal combustion conditions:

Mercury transformation during air-coal combustion has been simulated in both the absence and presence of fly ash particles. As expected from fundamental kinetic calculations, the coal chlorine results in 100 ppm of gas-phase HCl which contributes to less than 0.9 % of mercury oxidation in the gas phase in such temperature ranges (Fig. 1). Cao et al. [4] also concluded that in the absence of particles, mercury oxidation would be insignificant. The simulation was repeated in the presence of fly ash particles and mercury oxidation extent was found to increase to up to 2.5% (Fig. 1).

Figure 1 shows the comparison of the prediction from the CFD model with the reported experimental data from [4]. It is observed that the combined homogeneous-heterogeneous mechanism is capable of predicting the extent of mercury oxidation with good agreement to the experiment. It is envisaged that the discrepancy stems from ignoring sulphur and other species effect on the gas and solid phase transformation of mercury. As suggested in [3,4], with the addition of further amounts of HCl (or HBr which is proven more efficient in mercury oxidation), one would expect a higher level of oxidation in the slipstream reactor.

4.2. Oxy-coal combustion conditions:

When the simulation was performed for oxy-coal conditions in the absence of the fly ash particles, oxidation of mercury in the gas phase was predicted to be even lower than in the air-coal combustion. The reason is related to lower conversion of HCl to chlorine radicals (as the most important species for initiating gas-phase Hg^0 oxidation) calculated in oxy-coal combustion because of under once-through conditions. If the effect of recirculation was considered, a higher concentration of chlorine species in the flue gas would contribute to larger extent of mercury oxidation.

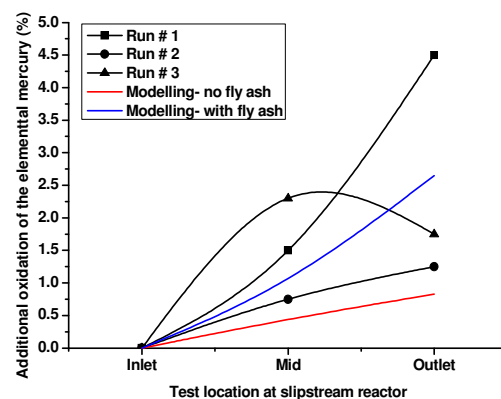


Figure 1: Comparison of measured and simulated mercury oxidation with 100ppm HCl in the absence and presence of fly ash

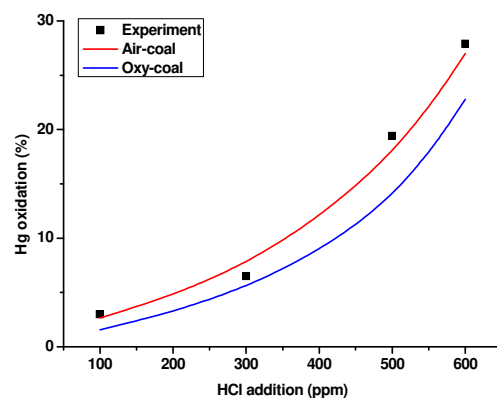


Figure 2: Comparison of mercury oxidation predictions at air-coal and oxy-coal combustion conditions

Figure 2 shows a comparison of mercury oxidation in the presence of fly ash in air-coal and oxy-coal combustion conditions with experimental data. Mercury oxidation in air-firing conditions is predicted with a reasonable accuracy and there is a slight reduction in Hg oxidation for oxy-coal combustion conditions. The reason for the similar predictions lies in the fact that fly ash specifications (size, burnout and mercury content) are assumed the same for both conditions since no measurements were available. It has been suggested by previous researchers [8,9] that one would expect a different carbon content of fly ash under air-coal and oxy-coal combustions. Mercury retained on the particle (Hg^P) is calculated from summation of Hg^0 and $HgCl_2$ that has accumulated on the fly ash. For a HCl concentration of 100ppm in both air-coal and oxy-coal combustion conditions, ~ 0.13 ppm of mercury was found to reside on the particle which is physically reasonable. Carbon content of fly ash directly affects mercury heterogeneous oxidation and therefore its selection as the input to the model would improve the predictions and provide a better understanding of mercury transformation under oxy-coal conditions.

5. Conclusions

A CFD model including a combined homogeneous–heterogeneous reaction mechanism for the prediction of mercury speciation in flue gases from air-coal and oxy-coal combustion has been developed and compared to experimental data. The mechanism includes recent updates on gas-phase kinetic reactions for Hg–Cl kinetic interactions. Mercury adsorption-desorption on fly ash particles has been studied using a Langmuir-Hinshelwood mechanism, fitted into Arrhenius type rate coefficients. The predictions from the CFD model for air-coal conditions are compared to measurements from a pilot-scale test facility and show reasonable agreement. The deviations for the predictions may be attributed to errors in mercury measurements or the influence of other species on the surface promoted oxidation.

Predictions of mercury transformation in oxy-coal combustion have been obtained. However, they depend on some of the input conditions about which little are known, such as the carbon and mercury content of fly ash.

6. Acknowledgements

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5. References

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