Sorption Mechanisms for Mercury Capture in Warm Post-Gasification Gas Clean-Up Systems

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Abstract

Trace elements such as As, Se, V, Ni and Cd, and especially Hg compounds, are difficult to control in gasification processes because of high temperature /pressure conditions and reducing atmospheres. This research project is concerned with the use of a *high temperature* sorbent for Hg^0 in gasifier off-gases. Experimental results show that, with some oxygen present, the sorbent captured more than 80% Hg^0 in the entrained flow reactor configuration, and up to 100% Hg^0 in the packed bed reactor configuration, where apparent de-activation was also observed. Temperatures were in the 850^{0}C – 1000^{0}C range. Theoretical work has focused on understanding, from fundamental considerations, how Hg products are bound in the solid substrate matrix.

Objectives

The purpose of this study is to elucidate mechanisms of interaction between certain trace metals, including mercury (Hg^0 and Hg^{2+}) and a paper waste derived sorbents (PWDS or more properly, MinPlus), a novel sorbent specially engineered, but currently manufactured in large quantities from residues from paper recycling processes. Data from both entrained flow and fixed bed reactors and *ab-initio* theory will be used.

Materials

Sorbent Properties
-**Mean diameter:** about 20 ㎛
-**Bulk density:** about 0.5 g/cm^3
-**Major components**:
$CaCO_3$(41%), Al_2O_3-$2SiO_2$ (29%), CaO(23%), others (7%)

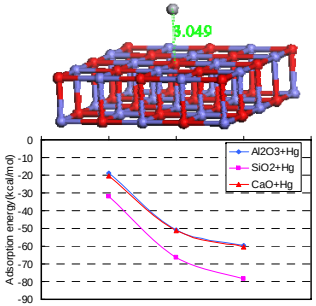
Mercury Source & Analyzer
PSA Elemental Hg Source
Tekran 2537A Hg Analyzer
: for low Hg Conc. <25 ㎍/m^3
Oil bath & VICI Hg Perm. Tube
Buck Hg Analyzer
: for High Hg Conc. >200 ㎍/m^3

Experimental Setup

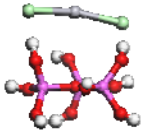
Fig. 1 Pictures of Entrained-flow reactor, Fixed bed reactor, and Hg Analysis System

Major experimental parameters for entrained-flow reactor (disperse phase) are test temp., sorbents feeding rate, residence time, and high (200 ㎍ /m^3)/ low (25 ㎍ /m^3) Hg^0 conc. condition. Fixed bed Hg experiments also carried out at different temperatures and sorbent loadings.

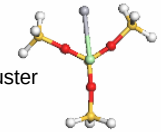
Theoretical Work



Accelrys DMol^3, DNP (double numeric with polarization) basis sets, restricted and unrestricted spin calculations, LDA with Harris approximation geometry optimization, energies at LDA with PWC functional and GGA with B LYP correlation functional.



Al_2O_3 T3 cluster with $HgCl_2$



SiO_2 T3 cluster with $HgCl_2$

Oxidized forms of mercury adsorb more strongly on all surface models – more work must be done to expand non CaO clusters

Conclusions & Future Work

A new disperse phase entrained flow reactor has yielded data suggesting that PWDS (or MinPlus) is very effective for Hg adsorption at high temperatures, although, insufficient dispersion of sorbent within the reactor may limit the capture observed. Capture is enhanced in the presence of oxygen. Temperature, residence time and sorbent feed rate are important, although at present, these effects may well be confounded by changes in dispersion and mass transfer resistance in the reactor. Future work will focus on mitigating dispersion issues in the flow reactor, on closing the Hg balance through measurement of the captured metal in the substrate, and on determining the effects of other gasification gas components such as CO_2, CH_4, COS, H_2 etc., in the hope that we can show that the presence of O_2 is not required in order for sorption to be effective. Mechanisms of Hg adsorption will be elucidated through surface analysis (I.e XAFS, XRD) complemented by computational efforts.

Acknowledgements

Joep Biermann, Ph.D., MinPlus Inc, Walnut Creek, CA
Jake Van Alstyn, Undergraduate, Dept of Chemical Engineering, University of Utah

Results & Discussion

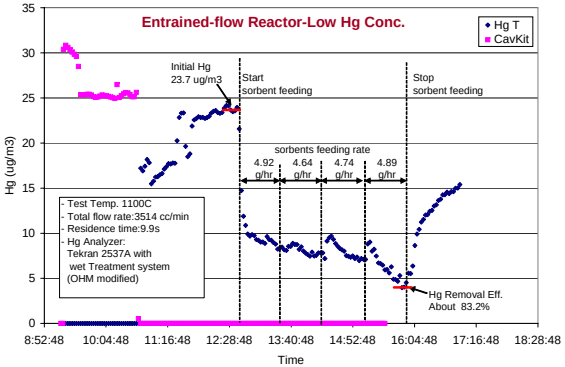


Fig. 2 Results of Hg adsorption test with entrained-flow reactor at low Hg concentration (for ~4 hours test)
Hg^0 react with sorbents rapidly and condensed sorbents in the reactor could affect the Hg removal continuously.

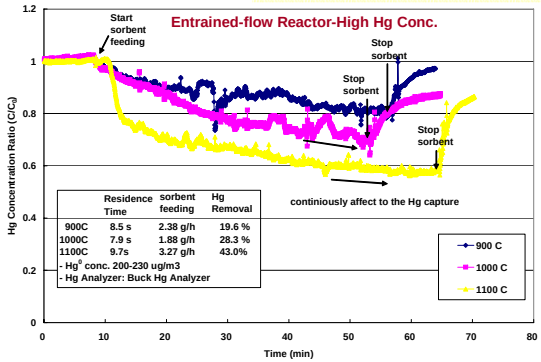


Fig. 3 Results of Hg adsorption test with entrained flow reactor at high Hg concentration (only for 1 hour test)
Hg removal efficiency depends on the sorbent's feeding rate, temperature, and residence time. (Hg conc. steadily decreased)

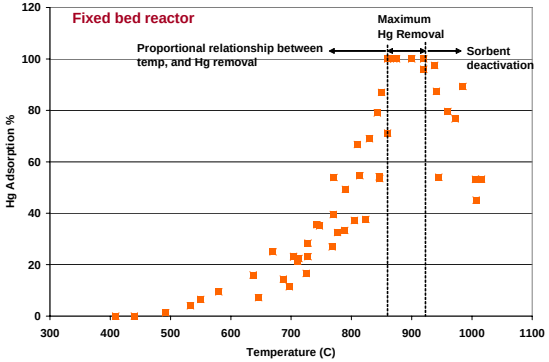


Fig. 4 Temp. effects on the Hg adsorption efficiency in the fixed bed reactor 870-920 C shows max. Hg removal efficiency. Hg adsorption decrease may be due to either sorbent deactivation or channeling and bypassing in the bed, due to sorbent shrinkage