SORPTION MECHANISMS FOR MERCURY CAPTURE IN WARM POST-GASIFICATION GAS CLEAN-UP SYSTEMS

Experimental and Computational Studies

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EXECUTIVE SUMMARY

Experimental Results: The removal of mercury vapors under high temperature combustion or gasification conditions is an important problem for coal combustion and gasification technologies. This work is concerned with sequestration of elemental Hg at high temperatures (900 - 1100°C) on a sorbent that is mineral based, rather than carbon based. This sorbent consists of an intimate mixture of CaO, CaCO₃, and Al₂O₃-2SiO₂, and is manufactured in industrially relevant quantities (metric tons) from residues produced by paper recycling processes. In contrast to activated carbon, this non-carbon based sorbent has special advantages in that it can actually enhance fly ash utilization for cement manufacture, rather than diminish it, as is the case for activated carbon.

Disperse phase experiments were conducted, using an externally heated quartz tube reactor, with sorbent feeding rates ranging from 1 g/h to 6 g/h. Experimental techniques, from the feeding of the sorbent to the measurement of ~μg/m³ levels of Hg²⁺, and Hg in the exhaust, are described in detail. Changes of mercury concentration in the reactor off gas were passed to a Tekran mercury analyzer with a wet bubbler system (modified by thiosulfate addition). The analyzer was calibrated by a Physical Sciences CavKit Hg calibration system. The entire Hg sampling, conditioning and analysis system were thoroughly validated in this and other contemporaneous mercury research programs. The temporal response of the reactor/sampling/ analysis system to sudden changes in input mercury levels was characterized. The sampling/analysis system had a response time in excess of two minutes, whereas the in flight residence time within the reactor was on the order of twelve seconds. Therefore temporal resolution finer than 2 to 4 minutes was not possible. In this work we denote *short time scale* processes or mechanisms as those that occur in times less than 4 minutes (the temporal resolution of our equipment), and *long time scale* processes as those that take longer than that.

Preliminary results indicated that Hg removal efficiency is sensitive to sorbent feed rates and to furnace temperature. The Hg removal percentage increased with both these variables. Subsequent experimentation showed that two mechanisms come into play: a *short time scale* (possibly, but not necessarily, in-flight) Hg sorption mechanism, and a *long time scale* Hg sorption mechanism related to sorbent deposits and their reactions with the quartz reactor wall. A maximum total (short time scale plus long time scale) Hg removal efficiency of 83-90% was obtained at temperatures of 900-1100 °C. There was negligible sorption by either mechanism at temperatures below 600 °C. Results for the short time scale mechanism alone showed a maximum sorption efficiency at ~900 °C, whereas the long time scale sorption efficiency involving reactions with the reactor surface increased monotonically with temperature. This suggests that sorbent de-activation can occur for the *short time scale* mechanism at high temperatures, which is in agreement with other fixed bed results obtained in this laboratory. Deactivation was not apparent for the sorbent related substance formed on the reactor wall. Raw and spent sorbents were analyzed by XRD and SEM-EDS to identify the sorbent mineral transitions that seem to activate the process, and analyses of the deposits appeared to confirm the sorption of mercury, although these data may have been obscured by gold coating interferences necessary for the EDS analysis .

The *short time scale* (less than 4 minutes in duration) mechanisms therefore appear to involve the following reactions:

- 1) activation of the sorbent, caused most probably by an internal solid-solid reaction, followed by
- 2) Hg sorption, and
- 3) de-activation if the temperatures are maintained at high levels for too long.

The *short time scale* mechanism, Reactions 1 through 3 above, is consistent with an in-flight mechanism, involving the sorbent and mercury only (no reaction with the quartz reactor or external SiO₂). It is also consistent with the Reaction sequence 1) through 3) above occurring on the wall, at longer solids residence times than the 12 second residence times available in the disperse phase, but shorter than the 2-4 minute interval that can be resolved by the Tekran and sampling train. The *long-time scale* mechanisms, possibly involving interaction with the quartz on the wall, still remain to be elucidated, but clearly involve creation of an active Hg sorption surface resulting from reactions between calcium species and quartz. De-activation was not observed for this long time reactor surface mechanism involving extraneous quartz.

A most important result was that both capture mechanisms (short time and long time) failed to occur in the complete absence of oxygen. It appears that previous results described in the original proposal were clouded by the (probable) presence of a small oxygen leak in the original packed bed apparatus. The current work has discovered that although some oxygen is required to allow the process to occur, the minimum amount of oxygen required might be as low as, and most probably much lower than, 4000 ppm. These results have important implications for the use of this sorbent in gasification processes, and these have been addressed in a companion volume to this Final Report. Experiments were also conducted to explore the effects of added water vapor, and although results here were somewhat ambiguous, the sorbent was still effective in the presence of water.

Another aspect that was explored related to effects of slight changes in sorbent composition. These results are potentially ambiguous and controversial, since the measured amounts of overall capture (short time scale processes plus long time scale processes) appeared to vary greatly from run to run for the same sorbent. Possible unavoidable reasons for this variation were inconsistent patterns of contacting between the sorbent jet and the walls. This sensitivity suggests that a key parameter might be the solids hold-up time (on or at the wall). This might have varied considerably from run to run because of small variations in the angle at which the sorbent exited the jet. These variations were at least as great as variations observed from sorbent to sorbent. However, since a significant amount of effort was expended to explore this facet of the problem, the results, although potentially ambiguous, are presented in detail.

In addition to the base sorbent (hereafter denoted as the Arizona sorbent) we tested several other samples of similar but not identical composition, but all arising from the same fluid bed combustion process. There was significant scatter in the data, and this was initially attributed to variations in the sorbent. However, continued experimentation showed that the scatter within the data obtained for one specific sample was at least as great as the scatter in the data between various sorbent samples. Therefore, the scatter in the data cannot be attributed to variations in sorbent composition alone, but rather to variations in how the sorbent interacted with the reactor

wall. Although there were significant differences in Hg sorption effectiveness through the *long time scale* mechanism, which required reaction with quartz in our reactor wall, examination of all the data allowed one to infer that the *short time scale* mechanism involved sorbent deactivation at ~1100 °C, yielding a maximum sorbent effectiveness through this mechanism at 900 °C. In our quartz reactor, the maximum capture achieved through the *long time scale* mechanism occurred for all sorbents at the highest temperature examined (1100 °C), but varied from 15% for the least effective run to 92 % for the most effective run.

For future work, it is recommended that quartz walled reactors *not* be used for high temperature entrained flow studies of sorbents containing CaO, or CaCO₃, because of reactions between SiO₂ (of the quartz wall) and the sorbent constituents. The long time scale deposit reactions, which then often dominate, are not easily reproducible, and also difficult to interpret quantitatively in terms of kinetic models, since they are influenced by deposition and re-entrainment transport mechanisms. Furthermore, these reactions involving the quartz walls may have little to do with wall reactions in field units, although they do suggest one mechanistic route through which an active Hg sorbent surface is created. We also suggest that the short time scale mechanism, involving sorbent only, be further investigated by experiments in which the sorbent hold-up amount, and also hold up time, within the reactor can be varied. One idea might be to increase the amount of sorbent deposited by inserting non-quartz-deposit surfaces internally within the reactor, so that the long time scale processes can be examined reproducibly in greater detail. Possibly, alumina or inconel walled reactors would be more suitable for subsequent studies in which the focus is on quantification of mechanisms not involving the reactor material.

Not all aspects of the pertinent mechanisms could be extracted from the experiments conducted in this project. First, the reactions with the quartz reactor wall produced confounding results, and allowed quantitative interpretation of only the short time scale mechanism, the magnitude of which was inferred (with mixed precision) from changes in mercury exit concentrations when the sorbent flow was shut off. Second, effects of variations in how the sorbent contacted the wall from run to run for the same sorbent, and also potential effects due to variations in sorbent composition, were not appreciated until the studies were fairly far along. A more complete understanding of which sorbent attributes may contribute to Hg capture is only now emerging.

Finally, it should be re-iterated that even though our understanding of pertinent mechanisms is incomplete, published results of two field tests (external to this research program) from two large bituminous coal fired combustion units have shown this sorbent to be very effective in removing mercury at high temperatures. The extent of in-flight versus deposit capture mechanisms in these field tests is not clear, although it is suggested that deposit capture dominated in those tests.

This research project has served to uncover many previously unknown factors that influence the use of *MinPlus* as a high or warm temperature sorbent in coal gasification and combustion systems. Not the least of these is our currently evolving hypothesis that solid/solid reactions within the sorbent, or between the sorbent and an external mineral can control the rate at which an active Hg sorption surface is created. These initial reactions of sorbent activation can occur in time scales of (up to, but less than) 4 minutes, defined here as short time scale processes (which show de-activation). Similar reactions can also occur in time scales of greater than 4 minutes, defined here as long time scale processes (which do not show de-activation). Specifically, this

research pointed to the potential importance of reactions between certain sorbent constituents and quartz, to produce active surface sites for Hg chemisorption in the presence of O₂. Future work is recommended in order to establish the validity of this hypothesis.

Theoretical Results:

The adsorption of Hg, HgCl and HgCl₂ on the CaO surface was investigated theoretically so the fundamental interactions between Hg-species and this potential sorbent can be explored. This surface was chosen as the starting surface model because it is easily modeled and because it is a large component of the MinPlus sorbent. Surface models of a 4×4×2 cluster, a 5×5×2 cluster and a periodic structure using density functional theory (DFT) calculations with LDA/PWC and GGA/BLYP functionals offer a useful description for the thermodynamic properties of adsorption on metal-oxides. The effect of temperature on the equilibrium constant for the adsorption of mercury-containing species on the CaO (0 0 1) surface was investigated with GGA/BLYP calculations in the temperature range of 250 – 600 K. Results show that at low coverage of elemental mercury, adsorption on the surface is physisorption while the two forms of oxidized mercury adsorption undergo stronger adsorption. The adsorption energies decrease with increasing coverage for elemental mercury on the surfaces. The chlorine atom enhances the adsorption capacity and adsorbs mercury to the CaO surface more strongly. The adsorption energy is changed as the oxidation state varies, and the equilibrium constant decreases as the temperature increases, in good agreement with data for exothermic adsorption systems.

DFT calculations were also used to investigate the mechanism of mercury adsorption on the paper waste derived sorbent (PWDS), MinPlus. Relaxed and rumpled CaO surfaces were employed as an improvement to the original calculations since rumpling and relaxation play an important role in evaluating adsorption energies of adsorbed species on oxide surfaces. The CaO component of PWDS was not a very strong adsorbent by itself to remove mercury-species in the prior work investigating adsorption of mercury-species on fixed CaO surfaces. However, the HgCl₂ adsorption models on the relaxed CaO surfaces in this work placed adsorption in the chemisorption range, although elemental mercury adsorption remained physisorption. The calculated adsorption values were -56.37, -35.69 and -31.26 kcal/mol on a 4×4×2 cluster, a 5×5×2 cluster and a periodic slab, respectively. The results of adsorption on the 4×4×2 cluster, however, are suspected of being incorrect due to edge effects through the limited size of the cluster compared to the adsorbate. On the 5×5×2 cluster and periodic slab, the adsorption energies of HgCl₂ were strengthened by ~ -20 kcal/mol compared with the fixed CaO surfaces. The relaxation effects strongly contribute to HgCl₂ adsorption while Hg and HgCl adsorption energies had little change due to the surface relaxation. The positive contribution of electron transfer in HgCl and HgCl₂ adsorption indicates that stronger adsorption occurs, and adsorbates are chemisorbed on the relaxed CaO surfaces. The results in this work indicate that the CaO component could be effective in capturing oxidized mercury, HgCl₂ promoted by chlorine in coal combustion flue gases.

Combined Results: We investigated the experimental and theoretical studies to understand the mechanism of the elemental mercury adsorptions on non-carbon based sorbents concerned with sequestration of elemental Hg on a sorbent that is mineral based, rather than carbon based at high temperatures (900 - 1100°C). Two mechanisms come into play in the experiment: an in-flight Hg sorption, and an Hg sorption mechanism related to sorbent deposits on the reactor wall. A

maximum total Hg removal efficiency of 83-90% within in flight and deposit related was obtained at temperatures of 900-1100°C. Results for the in-flight mechanism alone showed maximum sorption efficiency at ~900°C, whereas that on the reactor surface increased monotonically with temperature. Raw and spent sorbents were analyzed by XRD and SEM-EDS to identify the sorbent mineral transitions that seem to activate the process. The in-flight mechanisms appear to involve 1) activation of the sorbent, caused most probably by an internal solid-solid reaction, followed by 2) Hg sorption and 3) possible de-activation, if the temperatures are too high for too long. A theoretical study of Hg adsorption on a gehlenite surface which is a mineral transition product was also performed. In this modeling study, we proposed a complex structure and reaction steps for mercury adsorption to prove that an oxygen molecule plays an important role in improving the ability of elemental mercury adsorption on this sorbent according to the adsorption energy results. The presence of an oxygen molecule increases the adsorption energy of the elemental mercury on gehlenite from -16.7 kcal/mol to -30.3 kcal/mol.

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OBJECTIVES AND SCOPE

The research was directed towards a sorbent injection/particle removal process where a sorbent may be injected upstream of the warm gas cleanup system to scavenge Hg and other trace metals, and removed (with the metals) within the warm gas cleanup process. The specific objectives of this project were to understand and quantify, through fundamentally based models, mechanisms of interaction between mercury vapor compounds and novel paper waste derived (kaolinite + calcium based) sorbents (currently marketed under the trade name *MinPlus*).

The portion of the research described first is the experimental portion, in which sorbent effectiveness to scavenge metallic mercury (Hg^0) at high temperatures ($>600\text{ }^\circ\text{C}$) is determined as a function of temperature, sorbent loading, gas composition, and other important parameters. Levels of Hg^0 investigated were in an industrially relevant range ($\sim 25\text{ }\mu\text{g}/\text{m}^3$) although contaminants were contained in synthetic gases and not in actual flue gases. A later section of this report contains the results of the complementary computational results.

BACKGROUND

Coal is the most abundant fossil energy source in the world as well as in the US. Use of coal causes emission of global pollutants such as sulfur oxide (SO_x), nitrogen oxide (NO_x), carbon dioxide (CO_2), particulate matter (PM) as well as mercury (Hg). Hg control technologies have been the subject of considerable research because of that metal's high toxicity to human health and damage caused within the ecosystem [1].

The US Environmental Protection Agency (EPA), enacted the Clean Air Mercury Rule (CAMR) on March 15, 2005 to reduce total mercury emission from coal utilizing facilities through a 'cap and trade' system, which should reduce national utility emission of Hg from 48 ton/yr to 38 ton/yr by 2010, and to 15 ton/yr by 2018, when about 70% of the 2005 Hg emissions would have been removed [2]. Although CAMR was struck down by the District of Columbia Circuit Court of Appeals in February 2008, individual states and regions have enacted Hg control rules that are often more stringent than CAMR. Therefore, Hg control technology remains an important issue within the US.

Many studies have been focused on the development and evaluation of cost-effective and widely useable sorbents for Hg compounds from coal-fired power plant and gasification systems. To control the mercury compounds from coal utilizing facilities, including coal-fired power plant and gasification systems, adsorption processes have been widely employed. The commonly used adsorbates include activated carbon (AC), which has been injected as a fine powder upstream of ash particle control devices such as electrostatic precipitators (ESP), or fabric filters (FF) [1, 3-7]. However, the use of carbon-based sorbents is limited by their applicable temperature zone (below 300 °C) and by the ensuing deterioration of the quality of the fly ash for cement manufacturing [3].

Integrated gasification combined cycle (IGCC) is one of the alternatives to advance coal use for efficient electricity generation, and for production of useful by-products, such as hydrogen to be used in fuel cells [8, 9]. However, trace elements such as As, Se, V, Ni, Cd, and, especially, Hg compounds are quite difficult to control, because the gasification process is operated at high temperature/pressure conditions and under reducing atmospheres, resulting in most Hg compounds existing in their elemental form (Hg^0) [10, 11]. In general, Hg^0 is more difficult to control than ionic mercury (Hg^{2+}) because of its high volatility, low solubility in water and low reactivity with conventional adsorbents.

The components in PWDS are CaO 23%, $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ 29%, CaCO_3 41%, inert 6% and $\text{Ca}(\text{OH})_2$ 1%. Since CaO is one of the primary constituents in this novel sorbent that could be used in coal fired power plants, the adsorption of Hg, HgCl and HgCl_2 on the CaO surface were investigated so the fundamental interactions between Hg-species and the sorbent could be explored. Although there is no mercurous form of mercury (HgCl) in flue gases, we investigated adsorption of HgCl in order to compare with adsorption of Hg and HgCl_2 on CaO surfaces.

It is very difficult to examine the adsorption mechanisms of Hg-containing species on surfaces experimentally [12]. On the other hand, theoretical methods can be employed to investigate how Hg-containing species are adsorbed on the sorbent. The increase in computer speed and the accuracy of computational quantum chemistry methods leads them to be applied to the study of surface chemistry more frequently. Meanwhile, understanding

the adsorbents' surface properties theoretically will help us to choose the best adsorbent for certain adsorbates.

Since metal oxides are commonly used in industrial applications as catalysts or as support materials, structural and energetic properties of the metal oxide surfaces are important for understanding complex and comprehensive mechanisms. Many properties of metal oxide surfaces have been studied during the past decade [12-14]. The most prevalent compounds in PWDS are metal oxides. The CaO component chosen in this research, however, is the simplest rock-salt structure and has surface characteristics of alkaline earth metal oxides investigated by Broqvist, et al. [15]. Moreover, CaO can be an effective destructive adsorbent for small compounds such as fluoro-, chloro- bromo-carbons, sulfur- and organophosphorus compounds [16] .

EXPERIMENTAL METHODS AND MATERIALS

1. Entrained-flow reactor

High temperature mercury (Hg) adsorption experiments were completed using an entrained-flow type reactor. Two, three zone split tube furnaces (Thermcraft, Inc.) are installed vertically in series to control the reaction temperature, for which the maximum operating temperature is 1200 °C. In this experiment the temperature zone could be varied from 600 °C to 1100 °C by 100 °C increments. Figs. 1-3 show the schematic diagrams of the experimental set up and photographs of the resulting system.

The quartz reactor is designed and installed into the electric furnace for high temperature adsorption tests. The size of the quartz reactor is 50 mm O.D., 47 mm I.D, and 190 cm in length. It consists of three parts:

- 1) an upper top section for introducing sorbents, simulated flue gases, and elemental mercury,
- 2) a main body which has two sampling ports used for different residence times,

- 3) a bottom part for particle/gas separation, collection, and ventilation.

Figure 1. Schematic of dispersed phase reactor system.

Figure 2. Photographs of reactor. Clockwise: main reactor body, top section, bottom section.

A pre-heater is set to temperatures greater than 850 °C to heat the carrier gas before entering the reactor because the reaction temperature is over 600 °C and all of the gases must be pre-heated to reduce the heat transfer time in the reaction.

The reactor temperature range is 600 - 1100 °C. The flow of all gas components was controlled by calibrated mass flow controllers (MFC). Flow rates were checked before each experiment.

Figure 3. Left: Upper entry into reactor. Right: Inside the furnace, looking towards the top.

Table 1. Experimental flow rate and expected residence times¹

Total flow (L/min) at 800 °C	Required total flow (L/min) at 25 °C	Expected Residence Time (s) at 800 °C	Gas (cm/s) at 800 °C	velocity
30.0	8.3	5.5	28.8	
25.0	6.9	6.7	24.0	
20.0	5.6	8.3	19.2	
17.0	4.7	9.8	16.3	
15.8	4.4	10.5	15.2	
14.8	4.1	11.2	14.2	
13.8	3.8	12.1	13.3	
13.5	3.7	12.3	13.0	
13.0	3.6	12.8	12.5	
12.0	3.3	13.9	11.5	
11.0	3.1	15.1	10.6	
10.0	2.8	16.6	9.6	

¹ Values are calculated at 800 °C temperature, and shaded rows indicate experimental conditions attained in this study.

The inner temperature of the reactor was measured by insertion of a long thermocouple for each reaction temperature and flow range used. This characterized any temperature discrepancy between the furnace and the reactor.

The gas flow within the reactor is maintained as laminar flow. The settling velocity (terminal velocity) of sorbent in the reaction zone is considered and calculated by equation (1):

$$V_t = \frac{C \rho_p d_p^2}{18 \mu} g \quad (1)$$

Where, V_t is terminal velocity (or settling velocity), C is the drag efficient, d_p is the particle diameter, g is gravitational acceleration, and μ is gas viscosity. The calculated V_t of in these experiments is 0.6 cm/s. The Reynolds number is calculated following equation (2):

Figure 4. Photograph and schematic of ultra-low rate sorbent feeder.

$$R = \frac{\rho V D}{\mu} \quad (2)$$

The calculated Reynolds number for the reactor zone in the quartz tube is about 480 and about 54 in the sorbent's feeder. Therefore, the flow in the reactor could be regarded as having laminar flow conditions.

2. Sorbent feeder

The sorbent was injected into the reactor by a sorbent feeder wherein an aliquot of several grams of sorbent was loaded into a glass tube (1/2 "O.D), and moved by a syringe pump into the reactor with 0.5 L/min of nitrogen carrier gas. The sorbent feed rate of 2-7 g/hr was controlled by the frequency of vibration, the forward speed of the syringe pump, and the carrier gas flow rate to identify the effects of sorbent feeding rate on Hg adsorption ability at different reaction temperatures. Figure 4 shows schematics and pictures of the sorbent feeding system. The calibration curve for the sorbent feeder at various carrier gas flow

Figure 5. Calibration of sorbent feeder at various carrier gas flow rates.

rates is shown in Figure 5, and photographs of the overall feeding system are shown in Figure 6.

Figure 6. Photographs of the sorbent feeding system.

3. Hg analysis system

The mercury concentration in the outlet gas stream from the furnace was monitored by a cold vapor atomic fluorescence (CVAF) type Hg analyzer (Tekran 2537A) with a 4 channel sampling port. Elemental mercury was generated by a temperature controlled Hg^0 generator (Cavkit Hg calibration, PSA), which produces about $25 \mu\text{g}/\text{m}^3$, at a total flow rate of 2.2 - 4.7 L/min with compressed air. Figure 7 shows a picture of the Hg analyzer and elemental Hg source. The entire Tekran analyzer and Cavit Hg source system had been completely debugged in the course of other tests that were conducted in the same laboratory.

Before the start of each Hg adsorption test, an Hg balance check is carried out using the Hg generator and the Hg analyzer to verify the exact Hg concentration being generated by the

Figure 7. Tekran Hg analyzer with PSA Cavkit Hg source calibration system.

source, and then to check for any leaks within the reactor. After finishing the Hg balance checks, the experiments were commenced.

When an experiment is completed, the whole reactor including main body, top parts, and bottom parts were cleaned with soap, de-ionized (DI) water, and 10% HNO_3 solution in order to prevent any particle deposition and Hg contamination.

4. Hg treatment system

Hg speciation was determined on-line by a two set wet chemical impinger system.

One set of impingers contained SnCl_2 -HCl and NaOH solution in series for reading total mercury (Hg (T)) and the other set of impingers were filled with $\text{KCl-Na}_2\text{S}_2\text{O}_3$ and NaOH solutions in series to read elemental Hg (Hg^0) only. The role of the tin chloride (SnCl_2) solution is total Hg species reduction to its elemental form of Hg, and the purpose of the $\text{KCl-Na}_2\text{S}_2\text{O}_3$ solution is for elimination of oxidized Hg by absorption in solution.

The difference between Hg(T) and Hg^0 represents the oxidized mercury (Hg^{2+}) concentration. The schematic diagram of the Hg treatment system is shown in Figure 8 and picture in Figure 9.

Figure 8. Schematic of Hg treatment system.

Figure 9. Picture of Hg treatment system.

Figure 10. Field SEM images of kaolinite (left) and of *MinPlus* (right).

The sampling stream that is withdrawn is passed through a condensation chiller (Dual channel sample cooler Model 540, Universal Analyzers) to eliminate moisture before entering the Hg analyzer.

5. Sorbent Properties

Table 2. Summary of sorbent compositions [wt%]

Sorbent	Kaolinite [$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$]	Calcium Hydroxide [$\text{Ca}(\text{OH})_2$]	Calcium Carbonate [CaCO_3]	Major Impurities
Kaolinite	97%			1-2% TiO_2
Hydrated Lime		99%		0.2 FeO 0.3 Al_2O_3
<i>MinPlus</i>	45%	1% (22% CaO)	33%	0.1 TiO_2

In Figure 10 and Table 2, the mineralogical composition of one of the sorbents investigated here, and for brevity hereafter denoted as *MinPlus*, is compared to kaolinite (Fig 10 and Table 2) and hydrated lime (Table 2), which have been used in other studies. *MinPlus* is manufactured from a thermal process for which the feedstock is a solid by-product from paper recycling processes. As shown on Table 2, it is essentially an intimate mixture of kaolinite and lime/limestone sorbents. Kaolinite is a common mineral with many industrial

and commercial uses and its properties of have been well studied. Kaolinite is usually found to be composed of a series of stacked platelets. Figure 9 shows the typical structure of well-ordered kaolinite on the left, compared to the less structured morphology of *MinPlus*.

Of particular interest to this work is the process of calcination, which is a process whereby the chemistry and crystalline structure of a mineral is modified by exposure to increased temperatures [17]. *MinPlus* undergoes such a transformation at high temperatures. There

Figure 11. Differential thermal analysis of *MinPlus* sorbent. Note the mass-neutral structural transformations between 850 °C and 950 °C.

are two different calcination mechanisms: 1) ramp and soak calcination (typical of thermogravimetric analyses) where phase changes occur slowly, ultimately forming mullite, which is inert; and 2) flash calcination (typical of dispersed injection into a hot flue gas) where

heating is rapid, reaction times are short, and mullite formation is hindered. Therefore, one might expect the sorption reactivity of *MinPlus* to depend on the heat up process applied to it. Formation of mullite, which might be considered inactive for trace metal chemisorption, is hindered under rapid thermal processes occurring in short times, while it is favored in slower processes occurring over long times. Figure 11 shows results of differential thermal analysis of *MinPlus* (under ramp and soak conditions). These showed that this sorbent was reactive and responded to temperature changes. The trace with the various peaks shows heat taken in (endothermic) and given out (exothermic) from reactions that occur as a function of temperature. After initial fluctuations, the first peak is caused by Ca(OH)_2 conversion to CaO at approximately 400 °C, while the second peak describes CaCO_3 calcination to CaO and CO_2 , which is expelled at approximately 700 °C. Significantly, there are two mass-neutral conversions to (possibly) gehlenite and mullite occurring sequentially between 880 °C and 1000 °C. The most important conclusion to be drawn from Figure 11 is that the *MinPlus* sorbent is reactive over a wide temperature range, over which it undergoes important transformations. Some of these reactions are internal solid reactions/transformations which are often slow compared to gas/solid reactions, and may not occur under flash calcination conditions. These transformations are similar, but not necessarily identical, to those reported between a kaolinite and calcite mix by Traore et al., 2003 and Okala et al., 2003 [18, 19]. Fixed bed experiments reported elsewhere by Wendt et al., 2007 suggest that one of these transformations results in shrinkage of sorbent particles. Clearly, like its sister sorbent, kaolinite, *MinPlus* transforms chemically under the influence of heat and high temperatures

Several variations of *MinPlus* sorbent were investigated, each with slightly different elemental compositions and particle size distributions (obtained using Malvern PSD analysis), as shown on Figure 12 below. The “Arizona” sorbent had the widest particle size distribution, and the vast majority of experiments were conducted using it. A small number of experiments using the “June 06” and “May 07” sorbents were also completed. A summary of all runs completed using the quartz downflow reactor described above is included in this report.

MinPlus "Arizona" Sorbent

Al ₂ O ₃ (%)	14.4
CaO (%)	44.2
SiO ₂ (%)	23.1

MinPlus "June 06" Sorbent

Al ₂ O ₃ (%)	8.52
CaO (%)	52.2
SiO ₂ (%)	12.3

MinPlus "May 07" Sorbent

Al ₂ O ₃ (%)	7.36
CaO (%)	53.4
SiO ₂ (%)	9.90

Figure 12. Sorbent properties. Particle size distributions and compositions.

EXPERIMENTAL RESULTS

1.0 Reactor characterization

$\text{Hg}^0 \sim 25 \text{ mg/m}^3$; Sorbent flow $\sim 7 \text{ g/h}$, Sorbent conc. $67\text{-}73 \text{ g/m}^3$, $t_{\text{res}} = 15.8 \text{ s (1100}^\circ\text{C)} - 20.2 \text{ s (800}^\circ\text{C)}$

Figure 13. Typical temporal profiles of total Hg in the gas phase, measured in the exhaust. *MinPlus* "Arizona" sorbent.

Figure 13 depicts some typical temporal profiles of Hg (Total) in the exhaust. Data were taken over 200 minutes. Sorbent feeding was initiated at $t=0$. Sorbent feeding was turned off shortly after 60 minutes of run time. Experiments were conducted at temperatures of 800 °C, 900 °C, 1000 °C and 1100 °C, as shown. Residence times within the reactor varied from 15 to 20 seconds.

The first thing to note is that upon initiation of sorbent flow, the Hg signal decays, typically over a time scale of 20 minutes or longer. This is much longer than the gas phase residence time, as noted above. Upon shutting off the sorbent flow, the Hg signal in the exhaust can sometimes, but not always, rapidly jump up, over a time span of 2-6 minutes. Initially it was thought that this “rapid” increase in Hg could be interpreted as “in-flight” capture, and it has so been designated in several publications and presentations. However, it should be noted that even this “in-flight” capture can only be measured at best with a temporal resolution of 2 minutes, which is the temporal resolution for the Tekran measurements, and this resolution still lies outside the in-flight residence time of the sorbent in the reactor.

Figure 13 clearly shows two mechanisms at work, namely:

- 1) A short time scale mechanism, previously referred to as an “in flight” mechanism, but one that cannot exclude longer time scale phenomena occurring at the reactor walls. For the sake of brevity this short time scale process is designated “in flight” or “short time scale”, even though it may not be in flight and the time scale may well be over 2 minutes. These processes may involve deactivation and require a supply of fresh sorbent (to deposit) to continue. Hence they cease (after 4 minutes or so) when the sorbent flow ceases.
- 2) A long time scale mechanism, almost certainly involving slow reactions at the wall, probably between the deposits and the wall. This capture is the residual capture still observed when the sorbent flow is turned off, and sorbent deactivation is not observed.

We designate the process as “in-flight” and “deposit” capture, respectively, which is how they were initially interpreted.

The importance of the influence of the walls, and of the effects of sorbent deposition on the wall being a critical factor for both “short time scale or in-flight” capture and “long time scale or deposit” capture, was not appreciated until the experimental work was almost completed.

Figure 14. Summary of fraction of Hg captured from 19 runs with various *MinPlus* sorbent samples as a function of reactor temperature, °C.

Figure 14 shows a summary of the data collected using the quartz reactor. For each run the “in-flight” short time scale capture and the total capture, which is the sum of “deposit” long time scale capture and the former are shown. Through the considerable scatter, it is clear that two mechanisms are operative:

- 1) The short time scale capture which shows a maximum with temperature at 900 °C and deactivation at temperatures greater than 1100 °C, and
- 2) A long time scale capture that increases monotonically with temperature, dominating the total capture at 1100 °C

Some of the scatter in the data was initially attributed to variations in sorbent sample composition, and a significant effort was made to elucidate this. However, general, variations between sorbent samples were no greater than variations within one sorbent sample, although effects of changes in sorbent composition and particle size cannot be ruled out.

It is believed that deposition on the reactor wall plays a critical role, and that unavoidable variations of this process cause the scatter in the data shown on Figure 14. From day to day, and from experiment to experiment, it is extremely difficult to replicate exactly what

fraction of particles impact the wall, and how rapidly they are re-entrained. Small variations, and any roughness (caused by a sticky particle) at the particle nozzle exit can cause the particle flow to be asymmetric, with consequent variations in the fraction of the sorbent contacts the wall. Thus there were significant differences in Hg sorption effectiveness through the *long time scale* mechanism, which required reaction with quartz in our reactor wall. However, Figure 14 shows that all the data allowed one to infer that the *short time scale* mechanism involved sorbent deactivation at ~ 1100 °C. In our quartz reactor, the maximum capture achieved through the *long time scale* mechanism occurred for all sorbents at the highest temperature examined (1100 °C), but varied from 15% for the least effective run to 92% for the most effective run. Here “least effective” and “most effective” pertain to various runs both with different sorbents and also with the same sorbent. This variation therefore cannot be attributed solely to sorbent composition effects since it also occurs through different temporal histories of sorbent deposited on the walls.

The data presented below, however is believed to be from internally consistent experiments where these confounding effects were minimized.

2.0 Temperature and sorbent loading effects

Figure 15 shows the results of dispersed phase Hg removal tests at different reaction temperature and sorbent feeding rates. The temperatures on this experiment are 600 to 1100 °C with 100 °C increments, and the sorbent loading rate ranges from 2.6 to 6.5 g/hr. The overall Hg removal efficiency clearly increased with increasing sorbent feeding rate and reaction temperature, suggesting an overall *chemi-sorption* mechanism. These results show that the Hg removal efficiency of this non-carbon based sorbent depends on

- reaction temperature and
- sorbent feeding rate.

An overall maximum Hg removal, about 83 – 90 % was achieved at temperature range 900 – 1100 °C.

In interpreting these data it should be recognized that only a fraction of the sorbent interacts with the wall, and it may well be only that fraction that dominates the sorption process measured here.

Figure 15. Hg removal percent at various reactor temperatures and sorbent feed rates.

3.0 Short time scale (“in-flight”) capture and long time scale (“wall deposit”) capture

In the disperse phase experiments, the total removal efficiency could be obtained by means of short time scale “in-flight” capture and wall deposition effects (wall effects), as shown in Figure 13. It is important to distinguish from these observed short time scale “in-flight” capture and wall deposit effects for understanding and determining mechanisms of Hg adsorption at high temperatures.

Figure 16 shows a temporal trace of the mercury outlet concentrations as a function of run time during the experiment. These data are for sorbent feed rates of ~6.9 g/h. Figure 16 shows that capture (sorption) of mercury continues to increase over long time scales (i.e. 40

minutes), whereas the mean residence time of the sorbent in-flight in the reactor was on the order of 8 seconds. Clearly, the interaction between sorbents and the quartz wall attributed to Hg sorption, and the total capture reported from Figure 15, includes the results of two different mechanisms:

- 1) an “in-flight” or short time scale mechanism involving transformations within the sorbent (or a thermal derivative thereof) with subsequent sorption of Hg, and
- 2) a mechanism involving interactions between Hg and deposits formed on the

Figure 16. Temporal Hg trace after starting and stopping the MinPlus sorbent feed in the quartz reactor (total flow rate 2.2 L/min air, avg sorbent feed 6.87 g/h.

reactor walls. White scaly deposits were indeed observed and analyzed as shown below.

In Figure 16 the temporal trace of outlet Hg contains the results of both “in-flight” capture and capture on the reactor wall deposits. When the sorbent feed is turned off, the Hg outlet level immediately jumps up, which is attributed to “in-flight” capture, or at least capture occurring within the temporal resolution of the Tekran analyzer (2-4 minutes). From these results, it is furthermore apparent that “in-flight” capture of Hg is also affected by reaction temperature, but unlike the total capture (“in-flight” plus on-surface) it is a maximum at a temperature of about 900 °C. The in-flight sorbent then appears to undergo deactivation at high temperatures over 1100 °C. The on-surface capture, on the other hand, increases continuously with temperature. At 1100 °C the in-flight capture is almost zero, but the on-surface capture is 92 %.

These same data can be re-plotted to form the bar charts shown below in Figure 17. This demonstrates the activation of *MinPlus* at temperatures above 600 °C followed by a subsequent de-activation for the short time scale process. It is now believed that the short time scale process most probably requires a longer solids hold-up time than the ~20 seconds allowed by the gas residence time, and that the short time scale process is dominated by reactions within the sorbent itself (i.e no chemical reaction with the quartz reactor wall).

The long time scale mechanism, which does not undergo de-activation at high temperatures, involves a product of reaction between *MinPlus* and the reactor wall (SiO_2), with an excess of SiO_2 being present. This hypothesis received some support upon analysis of the white scaly deposit the formed. Furthermore, it is known that CaO (lime) will react with SiO_2 (quartz) at temperatures above 900 °C.

Figure 17. Hg removal efficiency through short time scale, "in-flight", and long time scale capture by deposits, "wall effect", at various temperatures.

4.0 The role of oxygen in the flue gas containing Hg

Fixed bed tests (not reported here) showed that the existence of oxygen (O_2) is essential for reaction between sorbent and elemental Hg. Data reported in previous publications showing success without O_2 present, may have been confounded by air leakage. Therefore, it was important to determine the sensitivity of the results to different O_2 concentration.

Figure 18. The effect of oxygen concentration on Hg^0 capture by MinPlus

The O_2 concentration was changed by mixing compressed air and nitrogen gas (N_2) using mass flow controllers to control compositions. The range of O_2 concentrations by volume ranged from 0.6 % (or 6000 ppm), 4.7 %, 16 %, and 21 %. Each O_2 concentration was maintained and measured by an O_2 analyzer (Model 100P, California Analytical Instruments) during the course of the experiment. Results are shown on Figure 18, showing the effect of O_2 concentration on Hg capture at 1000°C .

At 100 % N_2 there is negligible capture of Hg^0 , even at 1000°C . With only 4000 ppm O_2 in the nitrogen stream, there is over 80 % capture, although the process seems to occur on deposits and also seems to be quite slow (reaching a steady state at 150 minutes), The trace at 4.7 % O_2 is similar, but the rate appears to increase at the higher O_2 values.

Figure 19. The effect of water vapor (upper panel: 5% H₂O, lower panel 10% H₂O) on Hg capture by *MinPlus* in a stream containing O₂

Based on these test results it can be assumed that this non-carbon based high temperature sorbent requires just a tiny amount (probably less than 4000 ppm) of oxygen in order for sorption of elemental Hg to occur.

These experimental findings are important, since they may provide insight into the pertinent mechanism, and into the potential application to hot gas clean up in gasifier off-gases, where tiny amounts of oxygen might still be present.

5.0 The effect of water vapor

It is known that moisture contained in the flue gas can greatly influence physical and chemical adsorption processes. Therefore, experiments at two different moisture concentrations (10 % and 5 %) were carried out to identify the effects of moisture on Hg sorption by *MinPlus*.

Double de-ionized water was injected by a syringe pump at the exit of the pre-heater. The small water drops are quickly evaporated and then mixed with main carrier gas. All sampling lines were heated by heat-tape at 120 °C to prevent water condensation prior to entering wet-Hg treatment system.

Figure 19 shows the test results of the two moisture concentrations. Upon water injection, some of elemental Hg is oxidized, and the overall Hg adsorption might appear to be decreased when comparing to dry tests without moisture, see Figure 16. However, this decrease might be due to scatter in experiments (see Figure 14), which, in this case might have been exacerbated by the effect of water on wall deposition and adhesion. Alternatively, as shown by Liu et al, 2000, moisture can diminish a sorbents' adsorption capacity by blocking an entrance pore or occupying active sites on the surface.

6.0 X-Ray Diffraction (XRD) analyses of spent sorbent and EDX analysis of wall deposit.

It has been shown above that at a high temperature of 1100 °C the capture Hg “in-flight” or at short time scales was greatly diminished. In order to help identify the pertinent

mechanisms for both “in-flight” and “deposit” capture, XRD analysis of the raw and spent sorbent were compared, and SEM-EDX analysis of the scaly white deposit was performed.

Figure 20. Results of XRD analyses of raw (1) and spent (2) sorbent at 1100 °C

Figure 21. Results of SEM-EDS (a) surface morphology and (b) vertical line scanning of coated materials inside of the reactor

XRD patterns of raw sorbents (before experiment) and spent inflight (after experiment at 1100 °C) are shown in Figure 20. Calcite (CaCO_3), lime (CaO), and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_4$) peaks are dominant in the raw sorbent, while gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and calcium silicate peaks appear in the spent sorbent.

In this regard, Okada et al.[18], and Traore et al. [19], have observed the mineral transition between calcium compounds and kaolinite at high temperatures, and suggest that the following reaction is possible:

These observations suggest the importance of gehlenite as a potential active mercury sorption agent.

After several months of high temperature experimentation, a white unknown materials was collected from the inside of reactor, which was analyzed by SEM-EDS. SEM-EDS results of surface morphology (a) and line scanning (b) of a vertical cross section of a small fragment of coated material are shown in Figure 21. Some molten materials and the major elemental O, Si, Ca, Al, etc. could be observed in (a). Line scanning results also indicated that O, Si, Au, Hg, and Ca were major elements in (b). Although some mercury (Hg) peaks appeared in the SEM-EDS analysis, it is hard to identify final products of mercury compounds and its mass balance. The Hg levels automatically generated and shown on the left hand micrograph (b) seem abnormally high, and recent re-analysis has suggested that they may be an artifact caused by coating techniques. Additional work may be required to confirm these values since the qualitative presence of Hg in the wall deposits would be

important. Future work involving XAFS (x-ray absorption fine structure) analysis might shed light on the nature of the mercury compounds formed on the spent sorbents.

CONCLUSIONS FROM EXPERIMENTAL WORK

The research has led to the formulation of the following mechanistic hypotheses for mercury capture on *MinPlus*:

- 1) The first step is an *activation step* involving *MinPlus*. This occurs through at least two possible paths, namely:
 - a. Reactions of and between constituents contained *within* the sorbent at temperatures where calcination of CaCO_3 occurs. These may involve solid/solid reactions between a material containing Ca and another containing Si, although this has still to be confirmed. It is known that this activation step probably occurs in time scales on the order of minutes, rather than seconds. The products formed undergo *deactivation* at long times and/or high temperatures.
 - b. Reactions between sorbent constituents and *extraneous* SiO_2 at temperatures above 760°C . With an excess of SiO_2 , as provided by quartz reactor surfaces, the products formed from this process *do not* appear to undergo deactivation at *long times or high temperatures*. This solid/solid reaction is also slow, similar to the time scales in (a) above.
- 2) The second step is the *chemi-sorption* of mercury on an activated product formed through process 1-a or 1-b above. The mercury product is stable and has been shown to be released only at exposures for extended times to very high temperatures ($T > 1200^\circ\text{C}$) where the substrate disintegrates.
- 3) The third step is sorption de-activation, which appears to be caused by formation of a catastrophic melt that causes pore closure. As mentioned above, this catastrophic melt appears to be diminished under high excess (extraneous) SiO_2 conditions through reaction 1-b, where little de-activation has been observed. Several alkali metals (especially sodium) can greatly enhance the formation of a catastrophic melt involving kaolinite, which is present in *MinPlus*. PRB coals are known to have high sodium content and

low fusion temperature ashes, and these factors might have contributed to the poor performance of *MinPlus* observed with those coals.

Consistent with the mechanism above, the following additional conclusions may be made:

- 1) In general, mercury capture by *MinPlus* is often dominated by capture *on deposits* over *long time* scales. The detailed mechanism for this is complicated with both deposition and re-entrainment of sorbent occurring, probably with a wide distribution of sorbent residence times within the reactor.
- 2) Interpreting the sudden increase in Hg when sorbent feeding is stopped, as a short time scale mechanisms shows a maximum at 900 °C (close to the mineral transformation to form gehlenite, shown on the DTA).
- 3) Long time scale mechanisms involving deposit products formed between *MinPlus* and excess SiO₂ from the quartz wall provide Hg capture which increases with temperature, totally dominating the overall process at 1100 °C. This suggests that the high temperature capture of Hg by *MinPlus* is determined by mineral transformations of the sorbent at high temperatures.
- 4) XRD analysis of spent sorbent suggests reaction with quartz to form calcium silicate and calcium alumino-silicate compounds.
- 5) Additional results suggested that the presence of O₂, even as low as 4000 ppm (and possibly lower), was essential in order for either the in-flight or deposit mechanism to be operative.
- 6) Capture occurred in the presence of water vapor, although mechanisms might be affected.
- 7) All the experimental results reported here were affected by deposition and re-entrainment mechanisms on the reactor wall. These interactions of the sorbent with the hot reactor wall were difficult to reproduce from run to run. Future work on this sorbent should not employ quartz walled reactors.

COMPUTATIONAL CHEMISTRY METHODS

1. Density functional theory with LDA/GGA functionals and basis set

DFT has already been proved to be fairly robust [20] and can be used to calculate structural properties that are typically within 0.05 Å and 1-2° of experiment, while overall adsorption and reaction energies are typically within 5 – 7 kcal/mol of experimental values, and spectroscopic analyses are within a few percent of experimental data [21, 22]. However, it should be pointed out that the accuracy of DFT in treating the Hg transition metal system does have limitations since the system possesses spin multiplet structures that are energetically close to each other [23, 24].

Density Functional Theory (DFT) with the DMol³ [25] package in the Accelrys Materials Studio 2001 [26] was used for this portion of the work. All simulations for cluster and periodic CaO models used the AE (all electron) method and DND (double-numeric) basis set. DSSP (DFT semi-core pseudopotentials) and DNP (double-numeric polarization) were used for elemental mercury adsorption on the model surfaces. The local density approximation (LDA) combined with the PWC functional [27] was used with the Harris Approximation [28] in order to reduce the computational time for geometry optimizations. The generalized gradient approximation (GGA) was combined with the BLYP correlation functional [29-31]. The higher level calculations of the GGA/BLYP method used the fully optimized geometries from the LDA/PWC functional to obtain the adsorption energies. Mulliken and Hirshfeld population analyses were computed with the LDA/PWC method, not only to calculate atomic charges, but also to investigate how the mercury-containing species interact with the model surfaces.

Spin unrestricted calculations on the cluster models and spin restricted ones on the periodic slab were conducted because spin polarization could have an affect on the predicted adsorption energies. However, when we tested spin restricted and unrestricted methods for adsorption of the same species on the 4×4×2 surface, the Hg adsorption energy difference between the two calculations was ~ 0.5 kcal/mol, which is too small to impact our results. Spin-orbit coupling effects are neglected in this scalar relativistic approach based on prior research with other mercury calculations [32-34]. The numerical basis functions of DMol³

are more complete functions than Gaussian functions and are expected to have a small BSSE (the basis set superposition error) contribution while *ab initio* methods use BSSE calculations to estimate the errors associated with their incomplete basis sets [35]. A small BSSE contribution due to the basis sets of DMol³ was verified by Govind and Andzelm, et al., for calculations with a water dimer with a larger basis set. The interaction energy was changed by less than 0.5 kcal/mol in these calculations [36, 37]. They, indirectly, proved that further basis set extensions have a small BSSE effect on interaction energies.

2. Simulated surface models

The number of published papers employing CaO cluster models is quite limited, but some publications have appeared [15, 38-42]. Recent work on a similar cluster looked at NO_x and other compounds being adsorbed on a relatively small CaO cluster that was allowed to relax during the geometry optimization [43]. Other researchers used a fixed cluster approach [39, 40, 42]. There are some calculations on CaO surfaces, which are for much smaller adsorbates where more elaborate methods can be applied [39, 40, 42, 44]. It is already generally accepted that cluster models and DFT calculations, as employed in the present work, offer a useful description for the thermodynamic properties of adsorption on metal-oxides [45, 46].

The surface of CaO (0 0 1) which has been used by other theoretical researchers [38-40, 42] was investigated. It should be noted that the 3×3×2 cluster model had edge effects but the 4×4×2 and 5×5×2 cluster models succeeded in size convergence [47]. We claim the 4×4×2 and 5×5×2 cluster models are large enough to handle the adsorbates studied here. In this work, the clean perfect surface was modeled by a 4×4×2 cluster, a 5×5×2 cluster, and a periodic structure. The Hg coverages for the 4×4×2 and 5×5×2 cluster models are 6.25% and 4.0%, respectively, and Hg coverage for the periodic slab is 4.0% since the surface was designed with a 5×5 unit cell. These low coverages were used to approximate pure component adsorption on fresh adsorbates which would overestimate the results for aged systems. However, we also calculated the adsorption energies of elemental mercury at higher coverages on the CaO 5×5 periodic slabs in order to predict some trends in coverage. Two surface layers of metal-oxide were employed to investigate interactions between the adsorbate and surface [43, 48, 49]. For some calculations, all CaO (0 0 1) structures were

fixed with a bond length of 2.405 Å between every distance of Ca–O pair for rapid investigations of mercury adsorption. This bond length is the default for the CaO (0 0 1) cleaved surface in DMol³. The periodic system studied has a vacuum thickness of 10 Å. This distance was chosen to eliminate spurious interactions between the adsorbate and the periodic image of the bottom layer of the surface which would appear on the top of the 5×5 unit cell. Also, the *k*-point was set to the 2×2×1 mesh by Monkhorst-Pack scheme for the periodic slab. Upon completion of the fixed CaO surface, the surface models were allowed to relax and the computations were repeated to investigate how a more realistic surface would interact with the mercury-containing species.

We exported a unit cell of the amorphous gehlenite structure from ICSD to construct a periodic structure for the gehlenite work[50]. The gehlenite structure with a 7.69Å × 7.69Å area, which is the default for the gehlenite (0 0 1), was cleaved in DMol³. The employed periodic slab geometries were infinitely extended to avoid edge effects and to reduce computational time; these periodic calculations also had a vacuum thickness of 10 Å. Calculations were performed with 3×3×1 mesh *k*-points by the Monkhorst-Pack scheme and the surface was fixed during optimization.

3. Adsorption Energies and Thermodynamic Properties Calculation

The DFT adsorption energy was calculated through the following equation:

$$\Delta E_{\text{ads}} = E_{\text{Hg-species+surface}} - E_{\text{Hg-species}} - E_{\text{surface}} \quad (3)$$

where ΔE_{ads} is the adsorption energy, $E_{\text{Hg-species+surface}}$ represents the energy of the adsorbate species – surface, $E_{\text{Hg-species}}$ is the energy of the gas phase mercury – containing species, and E_{surface} is the energy of the isolated cluster, in kcal/mol.

The computed zero-point energy and frequencies from the quantum calculations were used to obtain the Gibbs free energy for the equilibrium constant [51]:

$$\Delta G_{\text{ads}} \approx \Delta E_{\text{ads}} + \Delta E_0 + T(\Delta S_{\text{vib}} + \Delta S_{\text{trans,rot}}) - kT \ln \left(\frac{P}{P_0} \right) \quad (4)$$

$$K_{\text{eq}} = \exp(-\Delta G / RT) \quad (5)$$

where the ΔG is the change of Gibbs free energy for the adsorption process, ΔE_0 is the zero-point energy change during the adsorption process, and ΔS_{vib} and $\Delta S_{\text{trans,rot}}$ are the vibrational and translational, rotational entropy changes of adsorption in cal/mol K. T is the temperature in K and R is the ideal gas constant in cal/mol K. k is Boltzmann's constant and the pressure terms cancel out.

ΔS_{vib} is derived from the vibrational partition functions containing the gas, clean surface and adsorbed system and $\Delta S_{\text{trans,rot}}$ is derived from the translational and rotational partition functions developed by Loffreda [51],

$$\Delta S_{\text{vib}} = -k \ln \left(\frac{Q_{\text{ads}}^{\text{vib}}}{Q_{\text{suf}}^{\text{vib}} Q_{\text{gas}}^{\text{vib}}} \right) \quad (6)$$

$$Q_{\text{ads,suf,gas}}^{\text{vib}} = \prod_i \frac{1}{1 - \exp^{-\theta_{\text{vib},i}/T}} \quad (7)$$

$$\theta_{\text{vib},i} = \frac{h}{k} \omega_i^{\text{ads,suf,gas}} \quad (8)$$

where k is the Boltzmann constant in J/K, h is Planck's constant in Js, and $\omega_i^{\text{ads,suf,gas}}$ are the frequencies of the adsorbed state, clean surface and gas phase mercury species, respectively.

$$\Delta S_{\text{trans,rot}} = -k \ln \left(\frac{Q_{\text{ads}}^{\text{trans}}}{Q_{\text{gas}}^{\text{trans}} Q_{\text{gas}}^{\text{rot}}} \right) \quad (9)$$

$$Q_{\text{ads}}^{\text{trans}} = A \left(\frac{2\pi M_{\text{gas}} kT}{h^2} \right) \quad (10)$$

$$Q_{\text{gas}}^{\text{trans}} = \frac{kT}{P} \left(\frac{2\pi M_{\text{gas}} kT}{h^2} \right)^{3/2} \quad (11)$$

$$Q_{\text{gas}}^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \frac{T^{3/2}}{\sqrt{\theta_{\text{rot},x} \theta_{\text{rot},y} \theta_{\text{rot},z}}} \quad (12)$$

$$\theta_{rot,x,y,z} = \frac{h^2}{8\pi^2 k I_{x,y,z}^0} \quad (13)$$

where A is the adsorption area, M_{gas} is the molecular weight of the gas, h is Planck's constant, σ is the number of energy minima when the molecule rotates, and $I_{x,y,z}^0$ is the reduced moment of inertia.

The calculated entropy and zero point energy data of Hg, HgCl and HgCl₂ adsorption on each surface were available in the temperature range from 25 K to 1000 K. The equilibrium constants were investigated in the 250 – 600 K temperature range for adsorption on the CaO surfaces and in the 700 – 1300 K temperature range for metallic mercury adsorption on the gehlenite surface as each temperature range is more experimentally relevant for real adsorption systems [52]. The above equations were used to obtain the Gibbs free energy and the equilibrium constant for different adsorption scenarios.

COMPUTATIONAL CHEMISTRY RESULTS

1. Hg-containing species adsorption on the fixed CaO surface

Three different coverages (4%, 8% and 12 %) of elemental mercury on the CaO periodic surface were conducted. Table 3 shows that low coverage leads to the strongest calculated adsorption energies. The adsorption energies are -6.53, -6.32 and 0.5861 kcal/mol when the coverage increases from 4%, 8% and to 12%, respectively. The calculations show that the best case scenario is at the lowest coverage. All adsorption models of mercury-containing species on the CaO cluster and periodic surface structures were therefore calculated at the low coverage limit of the model structures and had the following results.

Table 3. The adsorption energies on CaO Periodic slabs as Hg coverage increases calculated with LDA/PWC and GGA/BLYP functionals

	CaO(5×5 Periodic)		
	Hg (4%)	2Hg(8%)	3Hg(12%)
R(1Hg-O) Å	3.037	3.044	2.689
R(2Hg-O) Å		3.056	2.701
R(3Hg-O) Å			2.693
E _{ads} (kcal/mol)	-6.53	-6.33	0.59

Optimized geometries and adsorption energies

Hg consistently adsorbed on an atop site over the oxygen atoms on the surfaces and each chlorine atom gravitated to calcium sites according to the optimized geometries as shown in Figure 22. The distances between mercury and oxygen on 4×4×2 surface are 3.04 Å for Hg(0), 3.288 Å for Hg(+1) and 3.728 Å for Hg(+2) at the lower level calculation levels; the mercury atom is farther away from oxygen as the mercury is oxidized. However, the chlorine atom has shorter bond lengths to the calcium surface atoms: 2.787 Å for HgCl, and 2.854 Å and 2.952 Å for HgCl₂.

Figure 22. Representations of top views and side views of adsorption of Hg-species on CaO (001) surfaces with the LDA/PWC method. (a) Hg atom adsorbed on a $4 \times 4 \times 2$ cluster, (b) HgCl molecule adsorbed on a $5 \times 5 \times 2$ cluster, (c) HgCl₂ molecule adsorbed on a $5 \times 5 \times 2$ periodic slab. The mercury atom is given in gray, oxygen in red, calcium in green, chlorine in light green.

The adsorption energies of mercury-containing species on the modeled structures, investigated with LDA/PWC and GGA/BLYP methods were calculated with equation (1) and the results are in Table 4. Bond lengths and adsorption energies for each species in Table 4 indicate which species are more strongly adsorbed to the surface. Figure 23 shows the trends in adsorption energies for several mercury species on the model structures. The GGA/BLYP method using optimized geometries from the LDA/PWC method leads to more accurate adsorption energies, in general, as proved by other researchers [53-58]. Figure 23 shows the trends as the adsorption strength is changed for the different oxidation states. Metallic mercury, which is not reactive, has the weakest adsorption, with values of -7.51, -6.33 and -6.53 kcal/mol on the 4×4×2 cluster, 5×5×2 cluster, and periodic slab, respectively. The adsorption of elemental mercury on the 4×4×2 cluster, 5×5×2 cluster, and a periodic structure is attributed to be physical adsorption according to the fact that the adsorption energy of Hg(0) from the GGA/BLYP calculations falls into the physical adsorption range of about 6 kcal/mol [59].

Table 4. The optimized geometries and adsorption energies obtained with LDA/PWC and GGA/BLYP functionals from different simulated structures (4×4×2 cluster, 5×5×2 cluster and periodic slab). All energies are reported in kcal/mol.

	CaO(4×4×2)			CaO(5×5×2)			CaO(5×5 Periodic)		
	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂
LDA/PWC									
R(Hg-O) (Å)	3.040	3.288	3.728	3.095	3.250	3.453	3.037	3.255	3.438
R(Cl-Ca)1 (Å)		2.787	2.854		2.801	2.827		2.804	2.826
R(Cl-Ca)2 (Å)			2.952			2.829			2.831
GGA/BLYP									
E _{ads} (kcal/mol)	-7.51	-40.80	-16.38	-6.33	-37.00	-18.73	-6.53	-30.95	-11.93

Figure 23. Predicted ΔE_{ads} (kcal/mol) using different cluster sizes and adsorbate species calculated at the GGA/BLYP level using LDA/PWC geometry optimizations. The ΔE_{ads} predicted using the 4×4×2 cluster, 5×5×2 cluster, and periodic structure are close to each other.

The adsorption energy of HgCl which has a +1 oxidation state for mercury is -40.80 kcal/mol on the 4×4×2 cluster and the addition of two chlorine atoms to increase the oxidation state of mercury to +2 leads to a reduced value of -16.38 kcal/mol on the 4×4×2 cluster. Other cluster and periodic slab models have the same trends. The oxidized mercury in the form of HgCl₂ over metallic Hg has stronger adsorption energy values with -16.38, -18.73 and -11.93 kcal/mol on the 4×4×2 cluster, 5×5×2 cluster, and a periodic slab, respectively. These results suggest that CaO will be a stronger adsorbent for the reactive oxidized mercury species. Adsorption of HgCl leads to the strongest adsorption energies among mercury species because the HgCl molecule has one unpaired electron and this leads to strong interactions with the surface on each of the cluster and periodic models. The adsorption of HgCl on the CaO (0 0 1) surface is predicted to be through chemisorption [59] while the adsorption energies of HgCl₂ on the CaO surfaces are at the threshold between physisorption and chemisorption. The chlorine atoms released from HCl or Cl₂ in the coal combustion flue gas system greatly enhance the adsorption capability of the CaO according to these predicted results. The fact that fluoro-, bromo-, and chloro-carbons are destructively adsorbed on the CaO surfaces and that calcium oxides can be effective in removing halogenated carbons as shown by Decker, et al. is consistent with our results [16].

Temperature effect on equilibrium constants (on fixed CaO surface)

The effect of temperature on the equilibrium constants for the adsorption of mercury-containing species on the CaO (0 0 1) surface was investigated with GGA/BLYP calculations. Figures 24, 25 and 26 show the results in the temperature range of 250 – 600 K. These figures were generated by using the atomistic thermodynamic calculations described earlier [51]. Temperature has a stronger effect on the equilibrium constant for HgCl adsorption than for elemental mercury or HgCl₂. The adsorption energy changes for HgCl adsorbed on the surfaces are quite large as the temperature varies because the free radical energy of HgCl is more sensitive to temperature. The equilibrium constant having the steepest changes for HgCl adsorption versus temperature is, therefore, intuitive.

Figure 24. The predicted equilibrium constants for adsorption of Hg, HgCl and HgCl₂ on a 4×4×2 cluster as a function of temperature calculated with the GGA/BLYP functional. The results show similar trends of the equilibrium constant getting larger with decreasing temperature.

Figure 25. The predicted equilibrium constant for adsorption of Hg, HgCl and HgCl₂ on a $5 \times 5 \times 2$ cluster as a function of temperature calculated with the GGA/BLYP functional.

Figure 26. The predicted equilibrium constant for adsorption of Hg, HgCl and HgCl₂ on a periodic slab as a function of temperature calculated with the GGA/BLYP functional.

The equilibrium constants decrease as the temperature increases and the adsorption of all mercury species is more favored at lower temperatures. This is in good agreement with trends for exothermic systems [60]. Figure 25 shows that the two oxidized forms of mercury have stronger adsorption than elemental mercury on a $5\times5\times2$ cluster in all temperature ranges. However, the small equilibrium constants of all mercury species at high temperatures means that oxidized forms are not effectively adsorbed under these conditions. The equilibrium constants for HgCl_2 adsorption on the $4\times4\times2$ cluster and periodic slab are lower than Hg adsorption above some high temperatures as shown in Figures 24 and 26. However, oxidized mercury has positive adsorption trends on CaO surface models. Adsorption is likely to occur in combustion flue gases, although elemental mercury adsorption is going to be more favorable at low temperatures.

Electronic structure (charge transfer, HOMO & LUMO energy levels, and band gaps)

Charge analyses results depend on the methods used and show how electron density is partitioned. In order to understand the trends in atomic charge transfer, atomic charges with two different methods including the Mulliken and the Hirshfeld population analyses are compared. The Mulliken method is the most commonly used population method and the Hirshfeld population analysis is based on the deformation density on the free atom electron density [61]. The atomic charges for a fixed clean periodic CaO slab and CaO slabs reacted with Hg, HgCl and HgCl_2 were used to obtain the final Mulliken and Hirshfeld charges. The results of atomic charge transfer of the Mulliken and Hirshfeld methods are in Table 5 and atom numbers used in the analyses are indicated in Figure 27.

Table 5. Changed atomic charges based on Mulliken and Hirshfeld population analysis of Hg, HgCl and HgCl₂ adsorption models on fixed 5×5 CaO periodic slabs.

	Mulliken			Hirshfeld		
	CaO-Hg	CaO-HgCl	CaO-HgCl ₂	CaO-Hg	CaO-HgCl	CaO-HgCl ₂
Ca 7	-0.02	-0.01	-0.01	-0.04	-0.03	-0.02
Ca 8	-0.02	0.01	-0.01	-0.04	-0.02	-0.02
Ca 9	0.01	0.02	0.01	0.00	0.01	0.01
Ca 10	-0.02	-0.01	0.00	-0.04	-0.03	-0.12
Ca 11	0.01	0.02	0.01	0.00	0.02	0.01
Ca 12	-0.02	0.02	0.00	-0.04	-0.12	-0.12
Ca 13	0.00	0.01	0.01	0.00	0.01	0.01
O 17	0.01	0.01	0.02	0.00	0.01	0.01
O 18	0.01	0.01	0.02	0.00	0.01	0.01
O 19	0.01	0.01	0.02	0.00	0.01	0.01
O 20	0.01	0.06	0.02	0.00	0.03	0.01
O 30	0.00	0.03	0.04	0.00	0.02	0.03
O 31	0.00	0.00	0.01	0.00	0.01	0.01
O 32	0.05	0.06	0.04	0.03	0.04	0.02
Hg	-0.07	-0.29	-0.18	0.09	-0.16	-0.10
Cl 1		-0.17	-0.08		0.02	0.08
Cl 2			-0.08			0.08

Figure 27. The atom indices for HgCl₂ adsorbed on CaO periodic surface to indicate the charge transfer with the LDA/PWC functional

The Mulliken charges of the mercury atoms for Hg, HgCl and HgCl₂ on the surfaces are changed by -0.07, -0.29 and -0.18, respectively and the chlorine is negatively charged to -0.17 in HgCl and -0.08 in HgCl₂. On the CaO surface, the atomic charges of the near atoms with Hg, HgCl and HgCl₂ as adsorbates changed as adsorption occurred. The final

atomic charges of the calcium 7, 8, 10 and 12 atoms were changed by -0.02 after CaO – Hg adsorption. All charges on oxygen atoms were changed positively after CaO – mercury-species were formed. The adsorption of CaO – HgCl receives more charge transfer between HgCl and the CaO surface compared with the other mercury-species adsorptions. This is intuitive because the adsorption of HgCl is strongest because chemical bonding occurs, as described earlier.

The trends in the Hirshfeld charges are similar to the Mulliken charge results. The Hirshfeld charges of the calcium 7, 8, 10 and 12 atoms all changed by -0.04 for Hg adsorption, -0.03, -0.02, -0.03 and -0.12 for HgCl, and -0.02, -0.02, -0.12 and -0.12 for HgCl₂, respectively. This is consistent with the Mulliken charge analysis as the same calcium atoms of the surface interact with mercury adsorbates. Again, when the mercury is oxidized, it is charged more negatively. This result is in good agreement with the fact that adsorption becomes stronger when a larger charge transfers occur.

HOMO (the highest occupied molecular orbital), LUMO (the lowest unoccupied molecular orbital) energy levels and band gaps of Hg, HgCl and HgCl₂ adsorption models, and clean 4×4×2 and 5×5×2 CaO clusters were calculated with the GGA/BLYP functionals. HOMO, LUMO energy levels and HOMO&LUMO energy gaps are shown in Table 6 and Figure 28.

Table 6. The calculated HOMO, LUMO energy levels and band gaps with GGA/BLYP functionals (HOMO and LUMO energy levels are in Hartrees, and band gaps are in eV)

	CaO(4×4×2)				CaO(5×5×2)			
	cluster	Hg	HgCl	HgCl ₂	cluster	Hg	HgCl	HgCl ₂
HOMO	-0.091	-0.093	-0.106	-0.107	-0.089	-0.091	-0.099	-0.103
LUMO	-0.046	-0.047	-0.053	-0.089	-0.043	-0.044	-0.050	-0.083
Band gap (eV)	1.230	1.244	1.437	0.495	1.274	1.276	1.331	0.539

Figure 28. The plots in HOMO, LUMO energy levels and HOMO & LUMO energy gap for Hg, HgCl and HgCl₂ adsorptions on 4×4 and 5×5 CaO cluster models with GGA/BLYP functionals (HOMO and LUMO energy levels are in Hartrees, and band gaps are in eV)

The HOMO and LUMO energy levels decreased as the mercury is oxidized. The HOMO energy levels of HgCl₂ on both 4×4 and 5×5 CaO surfaces significantly drop. The smallest band gaps occur when HgCl₂ adsorption occurs on the CaO surface because the conduction band drops to a lower level while HgCl adsorption on the CaO clusters has the largest band gaps. When the chlorine atoms are adsorbed on top of calcium, this makes the metal oxide more metallic. Figure 29 shows the HOMO molecular orbitals for the fully optimized 5×5 CaO cluster model and Hg, HgCl and HgCl₂ adsorption on the 5×5 CaO cluster model. For the clean CaO cluster, the edge oxygen atoms have a high energy state and π^* molecular orbitals are formed from 4s(Ca) and 2p(O) atomic orbitals. When Hg is adsorbed on the surface, the shape of the HOMO did not change much compared to the clean CaO surface. The HOMO for HgCl adsorption was localized between the adsorbate and the middle of the surface and strongly interacted with the first layer of the surface while the LUMO was localized at HgCl₂ adsorptions of the surface. There is a degenerate set of occupied π^* molecular orbitals between the σ and σ^* orbitals for the HOMO of HgCl molecule. Occupied π^* molecular orbitals occur with the destabilization of HgCl bond and inhibit the stabilizing effect of the π bonding electrons. This lone pair destabilizing effect generates a HgCl molecule that is strongly bonded to the CaO cluster models. The HOMO energy levels of Hg and HgCl₂ are much lower and do not appear on the figures. When HgCl₂ adsorption occurs, it is difficult to identify how the molecule interacts with the surface from the figure. The density of states can show more clear interactions between the molecule and the surface.

Figure 29. The plots in HOMO molecular orbitals for fully optimized 5×5 CaO cluster model and Hg, HgCl and HgCl₂ adsorptions on 5×5 CaO cluster models with GGA/BLYP functionals

Figure 30 shows the total density of states (DOS) and the partial density of states (PDOS) for the adsorption of Hg, HgCl and HgCl₂ on CaO periodic surfaces and a clean CaO periodic surface. The DOSs were calculated using DFT LDA/PWC based on the CaO periodic slab model. The occupied states of the oxygen 2p lone pair electrons of CaO are located from -0.1 to 0 Hartree. The shapes of the DOSs after the adsorption of Hg, HgCl and HgCl₂ on CaO surfaces are similar. However, a new peak which is the bonding state between mercury and oxygen arises around -0.3 Hartrees after adsorbing the Hg-species on the CaO surfaces. This peak is the major difference between the clean periodic CaO surface and after adsorption of mercury-species. When HgCl is adsorbed on the surface, the DOSs between -0.5 and -0.55 Hartrees for HgCl bonding on the CaO surface are slightly

broadened. This is due to interaction of s orbitals with the surface. The DOSs of Hg and HgCl adsorption models have similar patterns and band gaps. On the other hand, the DOS after adsorbing HgCl₂ on the CaO surface has an extra peak around -0.175 to -0.1 Hartrees. The peak for the bonding state between the mercury and oxygen atoms for HgCl₂ adsorbed on the CaO surface is shifted to -0.1 Hartrees, and a peak of the conduction band is shifted to the Fermi level. This confirms that the LUMO energy level of HgCl₂ adsorption is lower than other adsorption models. More information for the equilibrium constants, ΔS (cal/mol K), and ΔG (kcal/mol) of Hg, HgCl and HgCl₂ adsorption on each cluster and periodic slab in the temperature range 250 – 600 K and changed atomic charges are provided in Appendix B.

Figure 30. Total density of states (DOS) and the partial density of states (PDOS) of the adsorptions of Hg, HgCl and HgCl₂ on CaO periodic surfaces and the pure CaO periodic surface with LDA/PWC functional: a) CaO 5×5 periodic surface, b) Hg adsorption of CaO 5×5 periodic surface, c) HgCl adsorption of CaO 5×5 periodic surface, d) HgCl₂ on CaO 5×5 periodic surface (Fermi level is set to zero)

2. Hg, HgCl and HgCl₂ Adsorption on the Relaxed CaO Surface

Optimized geometries and adsorption energies

The fully optimized geometries for Hg, HgCl and HgCl₂ adsorption models on the relaxed CaO 4×4×2 cluster, 5×5×2 cluster and periodic slab using the LDA/PWC method are

represented in Figure 31. The mercury adsorbates were initially placed horizontally on the surface with mercury oriented towards the oxygen site and the chlorine towards the calcium site. The mercury adsorbed on an atop site of the middle oxygen while chlorine bonds with the calcium site on the $5\times5\times2$ cluster and periodic slab after optimization. On the other hand, the mercury-containing species on the $4\times4\times2$ cluster adsorbed quite differently from the other models. The mercury species were shifted on the $4\times4\times2$ surfaces with mercury moved slightly from an atop site of oxygen and chlorine moved toward a hollow site. The results of bond lengths are listed in Table 7. The distances between mercury for Hg, HgCl and HgCl₂ and oxygen on the $5\times5\times2$ cluster were 3.339 Å, 2.507 Å and 2.284 Å, respectively. Mercury has a shorter distance with oxygen as mercury is oxidized for the $5\times5\times2$ and periodic model. The chlorine atom contributes to the shorter Hg – O bond although Cl gravitates further from the surface calcium; the bond lengths between Cl and Ca were 2.863 Å for HgCl and 3.023 ± 0.5 Å for HgCl₂ on the $5\times5\times2$ surface. The optimized geometries of mercury-species on the periodic slab have the same trends as the $5\times5\times2$ surface. Dissimilarly, the bond lengths of Hg – O bonds on the $4\times4\times2$ cluster become longer as the mercury is oxidized; the distance between mercury for Hg, HgCl and HgCl₂ and oxygen are 3.352, 3.772, and 4.147 Å. While this model led to longer bond distances, the energies indicate stronger adsorption energies than on the $5\times5\times2$ cluster and periodic slab models. The edge oxygen atoms are noticeably contracted and this strongly influenced the bond lengths and adsorption energies, showing that this cluster is not large enough to model this system. Interestingly, when Hg-species are adsorbed on the relaxed $5\times5\times2$ surface, the structural configurations of the adsorbates after optimization were different from adsorption on the fixed surfaces [62] and the relaxed $4\times4\times2$ surfaces. While the chlorine atoms were found closer to the fixed CaO surfaces and the relaxed $4\times4\times2$ surfaces, the mercury moved farther away in those results.

1) Optimized geometries of (a) Hg, (b) HgCl and (c) HgCl₂ adsorptions on 4×4×2 cluster

(a)

(a)

(b)

(b)

(c)

(c)

2) Optimized geometries of (a) Hg, (b) HgCl and (c) HgCl₂ adsorptions on 5×5×2 cluster

3) Optimized geometries of (a) Hg, (b) HgCl and (c) HgCl₂ adsorptions on periodic slab

Figure 31. The top views and side views of optimized geometries for Hg, HgCl and HgCl₂ adsorption models on the relaxed CaO 4×4×2 cluster, 5×5×2 cluster and periodic slab (red atom: oxygen, green atom: calcium, light green atom: chlorine and gray atom: mercury)

The adsorption of mercury-species on the 4×4×2 cluster and only Hg on the 5×5×2 cluster had negative relaxations, but mercury-species containing chlorine on the 5×5×2 cluster and periodic slab led to positive relaxations. The relaxation results are reported in Table 7, and the distance change between two consecutive layers after optimization and the initial default distance and percentages of the surface relaxation are shown. The distance change is defined as $\Delta d_{ij} = [z(M)_i + z(O)_i]/2 - [z(M)_j + z(O)_j]/2$. The percentages of $\Delta d(\text{\AA})$ relaxation values were -13.14, -11.56 and -11.10 % for Hg, HgCl and HgCl₂ adsorption models on the 4×4×2 surfaces, respectively. The percentages of the surface relaxation for Hg, HgCl and HgCl₂ adsorption on the 5×5×2 clusters were -10.69, 5.24 and 10.56 %, respectively. The negative relaxation was strongly influenced by the 4×4×2 cluster model and Hg adsorption on 5×5×2 surface, with contraction of the surface layer.

Table 7. The bond distances between mercury adsorbates on the surfaces calculated at the LDA/PWC level, adsorption energies with GGA/BLYP, the surface relaxation (Δd) and percentage calculated with respect to the default distance (2.405Å) from DMol are listed. To compare the results, the adsorption energies on fixed CaO surfaces are also listed below [62].

	CaO(4×4×2)			CaO(5×5×2)			CaO(Periodic)		
	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂
LDA/PWC									
R(Hg-O) (Å)	3.352	3.772	4.147	3.339	2.507	2.284	2.588	2.367	2.267
R(Cl-Ca)1 (Å)		2.85	2.909		2.863	3.018		2.915	3.055
R(Cl-Ca)2 (Å)			2.911			3.028			3.056
GGA/BLYP									
E _{ads} (kcal/mol)	-6.13	-75.73	-56.37	-6.48	-38.35	-35.69	-5.59	-29.79	-31.26
E _{ads} (kcal/mol) ^a	-7.51	-40.8	-16.38	-6.33	-37	-18.73	-6.53	-30.95	-11.93
Relaxation effect									
$\Delta d(\text{\AA})$	-0.316	-0.278	-0.267	-0.257	0.126	0.254	0.116	0.205	0.279
Relaxation %	-13.14	-11.56	-11.10	-10.69	5.24	10.56	4.82	8.52	11.60

E_{ads}(kcal/mol)^a : adsorption energies on fixed CaO surfaces

The adsorption energies are listed in Table 7. The GGA/BLYP adsorption energies of elemental mercury on the 4×4×2 cluster, 5×5×2 cluster, and periodic structure were -6.13, -6.48, and -5.59 kcal/mol, respectively, which places them in the physical adsorption range [59]. The modeled CaO structures are unfavorable for elemental mercury adsorption, even

when the relaxation effect is included. However, on the $5\times5\times2$ cluster and the periodic structure, the adsorption energies of oxidized mercury species fall in the range of $-30 \sim -40$ kcal/mol as chemisorption. The oxidized mercury formed with chlorine in the flue gases [63, 64] favorably enhances the adsorption ability of mercury on the relaxed CaO surface. The $4\times4\times2$ cluster has the same trends of adsorption energies of oxidized mercury but had adsorption energies that are twice as strong as the other surface structures.

There was no large difference in adsorption energies for elemental mercury and HgCl on fixed and relaxed calcium oxide surfaces; they had ~ 1 kcal/mol energy differences. The HgCl molecule has an unpaired electron which leads to strong interactions with the modeled fixed CaO surfaces.

In general, the effect of relaxation was small when adsorption was clearly in either the physisorption or chemisorption ranges according to the adsorption energies of Hg and HgCl. On the other hand, relaxation plays an important role in moving some mercury species over the threshold between physisorption and chemisorption. For instance, the adsorption energy of HgCl₂ on the $5\times5\times2$ rumpled cluster and the periodic slab are -35.69 and -31.26 kcal/mol, respectively, but are -18.73 and -11.93 kcal/mol on the corollary fixed surface. The relaxation effect moved the weak adsorption energy for the fixed surface to stronger adsorption on the relaxed surface. The adsorption energies of the oxidized mercury-species (HgCl and HgCl₂) on the relaxed $4\times4\times2$ cluster were -75.73 and -56.73 kcal/mol, respectively. These values were much stronger than -40.8 and -16.38 kcal/mol on the fixed clusters. In summary, the $4\times4\times2$ cluster has different trends for bond lengths, adsorption energies and rumpling direction compared to the $5\times5\times2$ cluster and periodic slab results. This shows that the $4\times4\times2$ cluster has edge effects and that the cluster might not be large enough to model adsorption for this system.

Temperature effect on equilibrium constants (on the relaxed CaO surface)

Figures 32, 33, and 34 show that the equilibrium constants for all mercury-species on the $4\times4\times2$ and $5\times5\times2$ clusters and periodic slab increase as the temperature decreases. This is consistent with these being exothermic systems [60]. When the results of HgCl₂ adsorption were compared with the equilibrium constants on fixed surfaces, the relaxation effect contributed to much more favorable adsorption at all temperatures. The ability to adsorb

HgCl_2 on the periodic slab approaches the same values for equilibrium adsorbability of HgCl at high temperatures. The high adsorbability of HgCl_2 is valuable for real flue gas systems because most of the mercury exists in the oxidized form of HgCl_2 , and not HgCl . The employed CaO surfaces were more appropriate for capturing the oxidized mercury than elemental mercury at all low temperatures. The equilibrium constants of the elemental mercury adsorption on CaO surfaces showed little temperature effects for ΔG over the temperature range of 250 – 600 K.

Figure 32. Representation of the equilibrium constants of Hg , HgCl and HgCl_2 adsorption on $4 \times 4 \times 2$ cluster vs. temperature effects. The adsorptions of the oxidized mercury species are favorable at low temperature.

Figure 33. Representation of the equilibrium constants of Hg, HgCl and HgCl₂ on 5×5×2 cluster vs. temperature effects. The adsorptions of the oxidized mercury species are favorable at low temperature.

Figure 34. Representation of the equilibrium constants of Hg, HgCl and HgCl₂ on the periodic slab vs. temperature effects. The adsorptions of the oxidized mercury species are favorable at low temperature.

Electronic structure (charge transfer, HOMO & LUMO energy levels, and band gaps)

Charge results from the Mulliken and the Hirshfeld population analyses show how electron density is partitioned among species on the surface. The Mulliken method is the most commonly used population method while the Hirshfeld population analysis is based on the deformation density on the free atom electron density [61]. The atomic charges for a relaxed clean periodic CaO surface and CaO surfaces reacted with Hg, HgCl and HgCl₂ are compared with the results from adsorption on the fixed CaO surfaces modeled in our previous work [62]. The results of atomic charge transfer of the Mulliken and Hirshfeld methods are in Table 8 and the atom numbers used in the analyses are indicated in Figure 35.

a) Atom indices for Hg adsorbed on 4×4 periodic CaO surface

b) Atom indices for HgCl₂ adsorbed on 5×5 periodic CaO surface

Figure 35. The atom indices on CaO periodic surface used to discuss the charge transfer with LDA/PWC functional

Table 8. Changed atomic charges based on Mulliken and Hirshfeld population analysis of Hg adsorption model on relaxed 4×4 CaO periodic slab and HgCl and HgCl₂ adsorption models on relaxed 5×5 CaO periodic slabs (data for atoms most influenced by atomic charge transfer).

	Mulliken			Hirshfeld		
	CaO-Hg	CaO-HgCl	CaO-HgCl ₂	CaO-Hg	CaO-HgCl	CaO-HgCl ₂
Ca 1	-0.01	0.01	0.01	-0.05	0.01	0.01
Ca 2	-0.01	0.03	0.04	-0.05	0.01	0.01
Ca 4	0.01	0.03	0.03	0.01	0.03	0.04
Ca 7	0.01	0.00	-0.01	0.00	-0.04	-0.03
Ca 8	0.01	0.00	-0.01	0.00	-0.04	-0.03
Ca 10	0.01	-0.02	0.01	0.00	-0.07	-0.10
Ca 12	0.01	0.01	0.01	0.00	-0.10	-0.10
Ca 14	-0.01	0.01	0.01	-0.05	0.01	0.00
Ca 16	-0.01	0.02	0.01	-0.05	0.00	0.00
O 17	0.00	0.02	0.01	0.00	0.01	0.00
O 18	0.00	0.02	0.01	0.00	0.01	0.00
O 26	0.11	0.01	0.00	0.06	0.01	0.00
O 30	0.00	-0.03	-0.05	0.00	0.01	0.00
O 31	0.00	-0.02	-0.02	0.00	0.00	0.00
O 32	0.00	0.16	0.16	0.00	0.10	0.11
Total surface	0.14	0.39	0.32	-0.06	0.08	0.02
Hg	-0.15	-0.26	-0.11	0.06	-0.10	-0.07
Cl 1		-0.13	-0.11		0.03	0.03
Cl 2			-0.11			0.03

The Mulliken and Hirshfeld charges of mercury-species on the relaxed surfaces contributed more positively than those on the fixed surfaces. In the Hirshfeld method, the total surface charges on the relaxed slab were partitioned more positively than on the fixed surface. The total surface charges for Hg, HgCl and HgCl₂ adsorption on the relaxed surface were -0.06, 0.08 and 0.02, respectively while they were negatively charged on the fixed surface. The positive contribution to the adsorbate during HgCl₂ adsorption on the relaxed surface led to an increase in the adsorption energies. The Hirshfeld atomic charges during HgCl adsorption on the relaxed 5×5×2 surface were mostly transferred at Ca10, Ca12 and O32 atoms with changes of -0.07, -0.1 and 0.1, respectively. Additionally, the Hirshfeld charges of HgCl₂ adsorption were partitioned at the same adsorbed sites with values of -0.1, -0.1

and 0.11, respectively. The atomic charges for HgCl_2 adsorption on the CaO after relaxation occurred were changed at the same sites from the fixed CaO surface but had different magnitudes of electron transfer for both Mulliken and Hirshfeld population analyses. HgCl_2 adsorption on a relaxed surface had stronger interactions, and the relaxation of the surface influences the adsorption energies. On the other hand, relaxation effects are small for Hg and HgCl adsorption on the surface; Hg and HgCl adsorption on relaxed CaO surfaces has similar trends for sizes of atomic charge transfer as the fixed CaO slab results. The charge transfer results of Hg adsorption on the relaxed surface showed negative contributions from the adsorbate to the surface indicating very weak adsorption energy.

HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) energy levels, and band gaps for the Hg, HgCl and HgCl_2 on clean $4 \times 4 \times 2$ and $5 \times 5 \times 2$ CaO clusters were calculated with the GGA/BLYP functional. HOMO, LUMO energy levels and HOMO&LUMO energy gaps are shown in Figure 36. The clean CaO cluster had π^* molecular orbitals which are formed from 4s(Ca) and 2p(O) atomic orbitals in a diagonal direction and the middle oxygen atom had the highest energy state due to relaxation effects. The HOMO and LUMO energy level decreases as the mercury is oxidized. However, different energy levels and band gaps were observed for the adsorption models for $4 \times 4 \times 2$ and $5 \times 5 \times 2$ CaO clusters.

On the $4 \times 4 \times 2$ model, Hg adsorption had the largest band gap and the band gaps decreased as mercury was chlorinated. When the HOMO & LUMO gap of the clean cluster surface was compared for the three mercury-species' adsorption, small changes in band gap values were revealed due to the strong edge effects; there was no difference in band gaps between the clean cluster and Hg adsorption model.

Figure 36. The plots of HOMO and LUMO energy levels and the HOMO & LUMO energy gap for Hg, HgCl and HgCl₂ adsorption on 4×4 and 5×5 CaO cluster models with GGA/BLYP functionals (HOMO and LUMO energy levels are in Hartrees, and band gaps are in eV).

On the other hand, the HOMO energy level of HgCl on the 5×5 CaO surfaces significantly drops. The largest band gap occurred for HgCl adsorption and the HOMO for HgCl adsorption was localized between the adsorbate and the middle of the surface through strong interactions with the first layer. There was a degenerate set of occupied π^* molecular orbitals between the σ and σ^* orbitals for the HOMO of the HgCl molecule. Occupied π^* molecular orbitals occurred with the destabilization of the HgCl bond and inhibited the stabilizing effect of the π bonding electrons. This lone pair destabilizing effect generated a HgCl molecule that was strongly bonded to the CaO cluster models. When the chlorine atoms were adsorbed on top of the calcium atoms of the surface, the LUMO energy levels dropped. Positive relaxation influenced oxidized mercury species adsorption by also significantly lowering HOMO energy levels. These results indicate that the HgCl₂ adsorbate had strong interactions

with the relaxed CaO surface, as much as HgCl adsorption, leading to similar adsorption energies.

3. Gehlenite model computations for metallic Hg adsorption phenomena

Optimized geometries, reaction steps and adsorption energies

The aluminum site was the best adsorption site among three different tested adsorption sites which were aluminum, silicon and oxygen for the gehlenite surface. We reported the best case of the elemental mercury adsorption in this report. The elemental mercury was started on top of a middle aluminum site of the surface before optimization, but it moved to the hollow site between silicon and aluminum atoms during optimization. When elemental mercury was adsorbed on the gehlenite surface, the adsorption energy was predicted to be -16.7 kcal/mol, which places it at the threshold between physisorption and chemisorption. The bond distance between aluminum and Hg was 2.214 Å. This value does not guarantee irreversible strong mercury adsorption reaction on the sorbent to remove elemental mercury from flue gases as suggested from the experimental data.

Therefore, we considered three consecutive reaction steps involving oxygen molecules as a possibly being more energetically favorable:

- 1) an oxygen molecule is dissociated on the gehlenite surface at high temperatures.
- 2) dissociated oxygen atoms form strong bonds with an aluminum atom on the gehlenite surface to make active sites for mercury adsorption.
- 3) and, an elemental mercury atom is adsorbed on the formed active site of the surface.

Figure 37 shows the series of steps hypothesized to be important for strong elemental mercury adsorption on a gehlenite surface, with the important atoms and surface sites detailed. The geometry optimization results and adsorption energies of these three steps were calculated and reported in Table 9.

Figure 37. The 3D views and top views of optimized geometries of Hg adsorption on gehlenite itself (a), dissociated oxygen molecule with Hg adsorption on gehlenite (b), dissociated oxygen atom adsorption on gehlenite (c) and Hg adsorption on activated gehlenite (red atom : oxygen, green atom : calcium, yellow atom : silicon, violet atom : aluminum, gray atom : mercury)

Table 9. The bond distances between mercury adsorbate and oxygen and between oxygen and aluminum on the active sites of the surfaces calculated by LDA/PWC, adsorption energies by GGA/BLYP are reported. The bond distance between mercury and oxygen of the gehlenite surface and adsorption energy is compared.

	Gehlenite-O	Gehlenite-O-Hg	Gehlenite(Al)-Hg
	LDA/PWC		
R (Al-O) (Å)	1.653	1.681	
R (Hg-O(Al)) (Å)		2.197	2.214
	GGA/BLYP		
E _{ads} (kcal/mol)	-127.592	-30.292	-16.700

When the elemental mercury was placed on the top of the oxygen molecule, it atom moved to a hollow site between silicon and aluminum, bonding with the oxygen atom. As a result, the oxygen molecule was dissociated. The bond distance of the oxygen molecule was changed from 1.558 to 3.452 Å when the elemental mercury adsorption occurred. The dissociated oxygen atom on the surface can be transferred to the next available surface site to adsorb other elemental mercury atoms. From this investigation, our hypothesized reaction steps were slightly modified to include:

- 1) oxygen molecule adsorption on the gehlenite surface
- 2) elemental mercury adsorption on the surface of step 1)
- 3) the oxygen molecule is dissociated
- 4) the dissociated oxygen atom is transferred to the next available site to adsorb the elemental mercury atom.

Investigations were done for the above reaction steps on the clean gehlenite surface.

In the first step, the oxygen atom was added on top of the aluminum atom of the previously optimized clean gehlenite surface and the bond length was 1.85 Å. After optimization, the bond length was shortened to 1.653 Å with a calculated adsorption energy of -127.592 kcal/mol. The active site formed after the oxygen atom absorbed on the gehlenite surface. The elemental mercury atom, placed on top of the oxygen atom was started at 2.1 Å from the surface before geometry optimization of the adsorption process, and moved to the hollow site between an edge aluminum atom and the adsorbed oxygen atom. The bond distance between aluminum and oxygen was 1.681 Å and the bond length between active oxygen and mercury atom was 2.197 Å. Although the bond lengths were slightly longer than at the starting point, the adsorption energy was -30.292 kcal/mol for elemental mercury adsorption on the active site. This value indicated that this adsorption is in the chemisorption range and oxygen atoms make adsorption more favorable, supporting the experimental observations.

Temperature effect on equilibrium constants (on a gehlenite surface)

Additionally, the temperature effects on the equilibrium constants were investigated with a broader range of temperatures. Since the first calculations were performed at 298.15 K, the results of the equilibrium constants were calculated using statistical thermodynamics in a higher temperature range. Table 10 shows the equilibrium constants, entropies and Gibbs free energies at 298.15 K and in the 700 ~ 1300 K (high temperature) range. The $\ln(K_{eq})$ and ΔG at 1200 K (900 °C) where the maximum in-flight capture occurred experimentally were 12.993 and -30.979 kcal/mol, respectively. These values show that adsorption is favorable at high temperature. The linear relation between temperature and the equilibrium constants are shown at Figure 38.

Figure 38. The temperature effects on the equilibrium constants on elemental mercury adsorption on activated gehlenite surface: when the temperature increases the equilibrium constant linearly decreases showing exothermic reaction.

The equilibrium constants decreased as temperature increases. Although the equilibrium constants dropped at higher temperatures, their values showed this reaction still occurred favorably at high temperatures. These values show that this adsorption is an exothermic [60] and irreversible reaction at high temperatures from the fact that the reaction is irreversible when the equilibrium constant is large [65]. The low equilibrium constant of 47.755 at 298 K indicates that the elemental mercury adsorbed on a gehlenite surface in the presence of oxygen is not desorbed to the atmosphere at low temperature. Although this is an exothermic reaction, the strong elemental mercury adsorption occurs at high temperatures due to the endothermic dissociation reaction of oxygen molecules, which has a dissociation energy of 117. 838 kcal/mol in the gas phase. This compensates for the overall energetics [66]. For comparison, the dissociation energy of O₂ decreases as O₂ adsorption on Au surfaces occurs; E_{dissociation} of O₂ on top of the pyramid Au surface is 28.364 kcal/mol and dissociation energy value on Au cluster surface is 32.515 kcal/mol [67]. The decreased dissociation energies compensate for the exothermic energetics of mercury bond . Hence, the ability to remove mercury significantly drops at very high temperatures above 1000 °C because this adsorption process is unfavorable at high temperatures including the required dissociation energy for oxygen molecules.

Table 10. The equilibrium constant, entropy and Gibbs free energy values are listed at room temperature and high temperature ranges (298.15 – 1300 K).

T(K)	1000/T	ln(K _{eq})	$\Delta S(\text{cal/molK})$	$\Delta G(\text{kcal/molK})$
298.15	3.354	47.755	2.332	-28.291
700	1.429	20.697	0.284	-28.788
800	1.250	18.317	-0.162	-29.116
900	1.111	16.499	-0.577	-29.506
1000	1.000	15.073	-0.963	-29.949
1100	0.909	13.928	-1.323	-30.442
1175	0.851	13.210	-1.578	-30.841
1200	0.833	12.993	-1.661	-30.979
1300	0.769	12.217	-1.978	-31.558

Electronic structure (charge transfer)

It can be shown through the results of charge analyses how electron density is partitioned. Atomic charges were calculated and compared in order to understand the trends in atomic charge transfer and electronic structures using the Mulliken and the Hirshfeld population analyses. The deformation density on the free atom electron density is applied on the Hirshfeld population analysis method while the Mulliken method is the most commonly used charge analysis method [61]. The atomic charges for four different geometry configurations such as clean periodic gehlenite structure, and gehlenite slabs reacted with the elemental mercury atom and consecutively reacted with oxygen and mercury atom were calculated to obtain the final Mulliken and Hirshfeld charge transfer with the GGA/BLYP functional and are shown in Table 11. Atom indices for Hg and O adsorbed on gehlenite periodic surfaces are indicated in Figure 39.

Figure 39. Atom indices for Hg on Gehlenite periodic surface to indicate the charge transfer with the GGA/BLYP functional

Table 11. Data for atoms most influenced by atomic charge transfer based on Mulliken and Hirshfeld population analyses of Hg adsorption model on a gehlenite periodic surface

	Mulliken			Hirshfeld		
	Gehlenite-O-Hg	Gehlenite-O	Gehlenite-Hg	Gehlenite-O-Hg	Gehlenite-O	Gehlenite-Hg
O 2	-0.03	-0.05	-0.01	0.01	0.01	0.00
O 3	-0.04	-0.05	-0.01	0.01	0.01	0.00
Si 10	0.05	0.11	0.02	0.04	0.10	-0.01
Ca 12	0.01	0.00	0.01	0.00	0.01	0.00
Si 13	0.08	0.11	0.02	0.05	0.10	-0.01
O 17	-0.03	0.01	-0.02	-0.03	0.02	0.03
Si 19	0.01	0.01	0.00	0.01	0.01	0.00
O 20	-0.03	0.01	-0.02	0.02	0.02	-0.02
Al 21	0.01	0.02	0.00	0.01	0.02	0.00
Al 22	0.14	0.07	0.04	-0.04	0.06	-0.07
Al 23	0.01	0.03	0.00	0.01	0.03	0.00
Al 24	0.46	0.36	0.04	0.07	0.03	-0.06
O 27/Hg 27	-0.76	-0.67	-0.04	-0.47	-0.49	0.18
Hg 28	0.16			0.31		
surface total	0.60	0.67	0.04	0.16	0.49	-0.18

The total Mulliken charges on the surfaces for the gehlenite surface with Hg, gehlenite surface with O, and gehlenite surface with O and Hg were 0.04, 0.67 and 0.60, respectively.

When we compared the results of adsorption energies, the more positive charge transfers occur from the surface to the adsorbate for stronger adsorption. For instance, the adsorption energy of Hg adsorbed on the gehlenite surface was -16.7 kcal/mol and the surface was charged by 0.04 while the adsorption energy of Hg on the gehlenite surface reacted with O was -30.292 kcal/mol with a total surface charge of 0.60. The results by the Hirshfeld method clarify that the positive charge transfer from the surface to the adsorbate leads to strong adsorption. The chemisorption model of Hg on the activated gehlenite surface after adsorbing O had a positively charged surface by 0.16 as well as the surface reacted with O having -127.592 kcal/mol for the adsorption energy with a 0.46 value for the total surface charge. On the contrary, the negative charge transfer from the adsorbate to the surface makes the interaction between the adsorbent and adsorbate weaker. The negative surface charge value, -0.18, of Hg adsorption on the gehlenite surface itself indicated that this adsorption is less favorable than on activated gehlenite surface.

The atoms influenced most on the gehlenite surface were Al 24, Al 22, Si 10 and Si 13 in Figure 39 after the elemental mercury adsorption occurred. This is intuitive because the closest atoms significantly affect the adsorbed atoms. Nevertheless, the charge transfer values were very small in Hg adsorption on gehlenite surface comparing on the activated surface. In the Mulliken method, the values of positively charged atoms were 0.01 – 0.04 and oxygen atoms were changed by -0.01 or -0.02. On the other hand, the closest aluminum and silicon atoms to the adsorbates after the mercury atom was adsorbed on the activated surface were charged positively by 0.05 - 0.46 in the Mulliken analysis. Other oxygen atoms of the surface were changed negatively by -0.03 ± 0.01 . The adsorbed oxygen atom accepted the electrons from the surface and was negatively changed by -0.76 where this value leads to strong interaction with the surface. It can be concluded that the oxygen atom adsorbed on the gehlenite surface at high temperatures influences strong mercury adsorption on this surface. Elemental mercury in the presence of oxygen has been experimentally shown to be strongly adsorbed on this sorbent at high temperature as discussed earlier in this work.

CONCLUSIONS FROM THE COMPUTATIONAL CHEMISTRY STUDY

DFT calculational methods were used to investigate the adsorption of mercury-species on the fixed and relaxed CaO surfaces with LDA/PWC calculations for the geometry

optimization and GGA/BLYP functionals for the adsorption energies. On the $4\times 4\times 2$ CaO cluster, the optimized geometries and adsorption energies were strongly influenced by negative relaxation and edge effects. The chlorine atoms moved closer to the calcium atoms of the surface compared to adsorption on the fixed CaO surfaces. On the other hand, when the oxidized mercury was absorbed on the relaxed CaO surface, the chlorine atoms gravitated to be on top of the calcium atoms and bent towards the bulk surface, leading to a shorter distance between mercury and oxygen. On the $5\times 5\times 2$ CaO cluster and periodic slab, optimized geometry features and adsorption energies had similar trends. The calculated adsorption energies of HgCl_2 adsorption were stronger by ~ 20 kcal/mol, placing them in the chemisorption range rather than being at the threshold between physisorption and chemisorption. This was due to the relaxation effects. However, adsorption energies of Hg and HgCl adsorption were not changed compared to the fixed surface calculations due to small relaxation effects. The temperature effects on the equilibrium constants showed that these mercury-species' adsorption phenomena were in agreement for trends of exothermic reactions. The charge transfer calculations showed adsorption trends as surface-to-adsorbate contributions of electron transfer. On the one hand, the negative contribution of Hg adsorption on the surface indicated that it had a small adsorption energy, and on the other hand, the positive contribution of electron transfer from the surface to mercury species in HgCl and HgCl_2 adsorptions indicated that stronger adsorption occurred and adsorbates were chemisorbed on the relaxed CaO surfaces. Finally, the CaO component of MinPlus sorbents could be a strong adsorbent to capture oxidized mercury in the form of HgCl_2 .

From the theoretical calculations, the gehlenite surface itself as a mineral transition product was not a strong adsorbent because its adsorption energy was on the border between physisorption and chemisorption. However, when elemental mercury was co-adsorbed with an oxygen molecule, the oxygen plays a role to increase the adsorption energy into chemisorption range at high temperatures. An oxygen molecule might activate the gehlenite surface at high temperatures in order to favor mercury adsorption. This is in good agreement with the experimental results where there is increased mercury removal efficiency with air flow involving oxygen molecules present in the system. We confirm that the adsorption is exothermic and irreversible due to the relationship between the equilibrium constants and temperature. However, the role of this substance on either the

activation or deactivation process for the in-flight mechanism is not yet clear. Future work should focus on quantifying the pertinent activation and deactivation mechanisms for the in-flight mechanism, and also on the nature of the activated product for the on-surface mechanism.

NOMENCLATURE

a	Specific contact surface (cm^{-1})
a_i	activity of I species (-)
C	gas phase Hg^0 equilibrium concentration at the gas-solid interface (ug/m^3)
c	Hg^0 concentration in the gas phase (ug/m^3)
c_{out}	Hg^0 outlet concentration to the reactor (ug/m^3)
c_0	Hg^0 inlet concentration to the reactor (ug/m^3)
c^*	gas phase Hg^0 equilibrium concentration at the gas-solid interface (ug/m^3)
K_{ads}	thermodynamic equilibrium constant (-)
k_d	overall mass transfer coefficient (cm/s)
L	bed thickness (cm)
M	molecular weight (g/mol)
p	total pressure (Pa)
R	gas constant ($\text{J}/\text{mol K}$)
r	Hg^0 adsorption reaction rate ($\text{ug}/\text{Nm}^3 \text{ s}$)
T	absolute temperature (K)
t	time (s)
u_0	superficial velocity of the gas in the bed (cm/s)
z	axial coordinate along the reactor (cm)
ΔE_{ads}	adsorption energy (kcal/mol)
E	the total energy (kcal/mol)
ΔG_{ads}	the change of Gibbs free energy (kcal/mol)
ΔE_0	the zero-point energy change (kcal/mol)
ΔS	the entropy (cal/molK)
k	Boltzmann constant (J/K)
P_0	the initial pressure (Pa)
K_{eq}	equilibrium constant (-)
Q	partition function (-)
h	Planck's constant (J/s)
$I_{x,y,z}^0$	reduced moment of inertia (-)
A	adsorption area ($\text{\AA}^2$)
Δd	the change of distance ($\text{\AA}$)

z distance between metal atom and oxygen (Å)

Greek symbols

α constant in the Freundlich equation

β exponent in the Freundlich equation

ε void fraction of the bed (-)

η Hg0 removal efficiency (-)

ρ_p particle density (g/l)

ω adsorbate loading (g/g solid)

θ_{vib}

σ number of energy minima

ω_i vibrational frequency

π mathematical constant

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SORPTION MECHANISMS FOR MERCURY CAPTURE IN WARM POST-GASIFICATION GAS CLEAN-UP SYSTEMS

Modeling Support for Surface Reaction Mechanisms and Extrapolations to Gasifier Operating Conditions

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EXECUTIVE SUMMARY

This report was prepared under the Contract Agreement entitled “Sorption Mechanisms for Mercury Capture in Warm Post-Gasification Gas Clean-Up Systems.” This project is being conducted by Niksa Energy Associates LLC (NEA) under a subcontract to the University of Arizona, as part of their prime contract to the National Energy Technology Laboratory (NETL) under contract no. DE-FC26-04NT42313. NEA’s original role was to use simulations to bridge the gap between performance tests at atmospheric pressure with an Hg control sorbent called MinPlus and the intended application of MinPlus for Hg control in warm gas cleaning systems on coal gasifiers. Once the lab tests at U. Utah established that MinPlus can only be used in the presence of O₂, a new, stronger imperative emerged. NEA therefore re-directed its efforts to identify a scheme that could introduce the required O₂ level into a stream of syngas, and maintain it throughout the time needed to remove Hg on MinPlus. This is a deeper challenge than the original assignment because syngas and O₂ do not normally co-exist at typical MinPlus operating conditions for gasifier applications: MinPlus can only be used from 650 to 850°C; pressure is variable from 20 to 50 atm; and at least 0.5 s are needed for Hg removal.

NEA’s proposed scheme uses a bank of fixed beds to continuously generate low levels of O₂ in syngas, followed by a second series of fixed beds of MinPlus to capture Hg. Fixed beds provide the only means to uniformly disperse O₂ into the entire syngas stream while maintaining its concentration well below the explosion and flammability limits, which is imperative to avoid significant adverse impacts on the quality of the syngas. The MinPlus is also applied in a fixed bed configuration because this approach offers extremely high surface area to volume ratios to satisfy the constraint on the total Hg removal time.

The scheme utilizes BOC’s CAR process to uniformly introduce sufficient O₂ to maintain MinPlus’s Hg sorption activity. This process directly releases O₂ from Perovskite packing which is regenerated via counterflow oxidation with O₂. By simultaneously operating manifolds of beds in the O₂ generation and regeneration modes, the O₂ level in syngas can be maintained continuously. This process is already under commercial development for oxyfuel furnaces to raise the O₂ level in recycled flue gas above the level in air. In fact, the required O₂ generation capacity for the application of MinPlus in gasifier cleaning systems is slightly smaller than that for the oxyfuel applications, and commercial designs are already available to satisfy this requirement.

Most important, we found that the O₂ lifetimes in syngas from Shell and GEPS gasifiers provided sufficient time for Hg sorption on MinPlus, based on a detailed reaction mechanism for syngas reforming. For Shell gasifier conditions, up to 0.5 s was available for Hg sorption for temperatures up to 700°C. And for the very high operating pressure of GEPS gasifiers, the O₂ levels reached a stable saturation limit that persisted for at least 2 s provided that the temperature was no hotter than 700°C. The limit was 170 ppm O₂ at 700°C but only 70 ppm at 600°C. The limit's existence was found to be governed by elevated pressure, and limits only appeared for the GEPS cleaning system. Changing the O₂ injection rate off the baseline value of 1 % of the syngas stream did not elevate these saturation limits. Adverse impacts of O₂ injection on syngas quality were minimal, because the O₂ injection rates were so small; whereas the CO mole fractions diminished slightly the H₂ mole fractions increased for most conditions.

BOC's CAR process to generate O₂ from Perovskite minerals is already developed for oxyfuel applications. However, a major uncertainty is whether or not syngas components will react heterogeneously with oxidized Perovskites under MinPlus operating conditions. It also remains to be demonstrated that Perovskites may be regenerated with O₂ under hot gas cleaning conditions without steam washing. In addition, both equilibrium Hg adsorption capacities and intrinsic sorption kinetics need to be monitored for temperatures from 600 to 750°C at elevated pressures to provide the rate data needed to design a fixed bed of MinPlus.

Since NEA did not have access to the lab-scale kinetic data needed to pursue a preliminary design of a MinPlus bed for Hg control in gasifier streams, we demonstrated the extrapolations needed to scale-up Hg control with MinPlus from lab-scale to pilot-scale furnaces, rather than for gasifiers. Somewhat unexpectedly, there were problems in the simulation results for baseline tests, without MinPlus injection. These were rectified by adjusting the gas cleaning conditions. Ultimately, the MinPlus sorption kinetics specified by interpreting the lab-scale breakthrough tests were used without tuning to accurately predict MinPlus performance across a FF in the pilot-scale tests.

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1.0 SCOPE AND OBJECTIVES

This report was prepared under the Contract Agreement entitled “Sorption Mechanisms for Mercury Capture in Warm Post-Gasification Gas Clean-Up Systems.” This project is being conducted by Niksa Energy Associates LLC (NEA) under a subcontract to the University of Arizona, as part of their prime contract to the National Energy Technology Laboratory (NETL) under contract no. DE-FC26-04NT42313. Research objectives were defined under a statement of work that stipulated the following two tasks:

- (1) Propose and evaluate elementary surface reactions for Hg^0 sorption on kaolinite/lime based sorbents under reducing conditions, and validate the mechanisms in quantitative interpretations of project data on Hg sorption at atmospheric pressure. Also extrapolate the predicted sorption behavior to elevated pressure.
- (2) Extrapolate the Hg sorption to commercial gasifier operating conditions, and survey a broad domain of coal quality and gasifier operating conditions, including wide ranges of gas composition, pressure, and temperature.

The original purpose of NEA’s participation in this project was twofold: (1) Interpret the lab-scale sorption test data from Prof. Jost Wendt’s laboratory at the U. of Utah with a detailed surface reaction mechanism based on Prof. Paul Blowers theoretical surface species calculations; and (2) Extrapolate from the test conditions, particularly from atmospheric pressure, to gas cleaning conditions downstream of commercial coal gasifiers, and survey broad ranges of operating conditions.

However, this purpose was changed once the lab tests determined that the Hg sorbent would only function in the presence of molecular O_2 , which is nominally incompatible with the intended application to syngas streams. Although the tests did not precisely determine the minimum O_2 level for satisfactory sorbent performance, they found good Hg capture with 0.4 % O_2 and no capture with no O_2 . At that point, Prof. Wendt instructed S. Niksa of NEA to develop a processing strategy that would enable the original sorbent to be used with coal-derived syngas in the downstream gas cleaning section of a coal gasification system. In turn, the new goal was pursued in two revised project tasks: (1) Identify operating conditions in which sufficient O_2 levels could be maintained while Hg was captured on sorbent from syngas streams; and (2) Use NEA’s existing Hg transformation mechanisms to demonstrate how the process could be scaled to commercial applications.

Chapter 2 presents a processing strategy for Hg sorption from syngas streams and Ch. 3 presents the scaling demonstration. A fourth chapter surveys the findings and recommends ways to refine the analysis.

2.0 A PROCESS TO MAINTAIN APPRECIABLE O₂ LEVELS IN WARM SYNGAS STREAMS

Only a single sorbent, whose commercial tradename is MinPlus, was evaluated for Hg control under this project. This Ca-aluminosilicate material has two distinctive properties that must be managed in any practical application for Hg control. First, the material undergoes several important phase transformations including an essential calcining step that converts CaCO₃ into CaO at 600 - 800°C, and a catastrophic transformation into a mullite/ gehlenite melt at 850 - 950°C (Wendt et al. 2005). Prior to calcination, the activity for Hg control is minimal, whereas the transformation into mullite essentially eliminates the Hg sorption activity. Hence, this sorbent can only be used in the temperature window from 650 - 850°C. The second distinctive property is that the material adsorbs Hg only if O₂ is present in the process stream. Satisfactory Hg sorption was demonstrated in tests at U. Utah under this project for O₂ levels as low as 0.4 %, although tests with no O₂ present did not record any Hg capture. So we know that low O₂ levels are sufficient, but have not yet precisely determined the minimum O₂ level that sustains satisfactory Hg sorption.

To accommodate these properties, an adequate O₂ level must be maintained in syngas for the duration of Hg capture without adversely affecting the syngas quality. A process to satisfy these objectives is described in the next section, followed by a thorough evaluation of the lifetime of O₂ in syngas from two commercial entrained flow gasifiers, one from Shell and the other from General Electric Power Systems (GEPS). Other essential technical specification are discussed to bolster the feasibility of the process.

2.1 MinPlus Implementation Strategy

Under the vast majority of hot gas cleaning conditions, syngas and O₂ cannot co-exist. This is certainly true if these two components are present as a combustible mixture. But the rich flammability limits for premixed flames of H₂ and CO are both 74.2 % (Kuo 1986), which requires more than ten times the nominal 0.4 % O₂ needed to activate MinPlus. Even so, flammability considerations dictate that the O₂ must be introduced into the syngas stream within the MinPlus temperature window, in such a way that no local flammable mixtures are generated. Ideally, the O₂ would be injected volumetrically throughout the entire cross section of the syngas stream, so that the local O₂ level would never exceed the target value.

Even without a flame, any O₂/syngas mixture will react volumetrically provided that the temperature is above an ignition threshold, which is above about 500°C. This

Figure 2-1. The proposed scheme for syngas application with MinPlus.

decomposition must be managed to ensure that the O_2 survives long enough to activate the sorbent while it removes most of the Hg from the syngas stream. In other words, the Hg sorption rate should be maximized, to ensure that the O_2 levels remain high enough to activate the sorbent. Finally, the impact of the Hg control technology on syngas quality must be minimal. It is certainly not practical to consider any scheme that requires depressurization of the syngas stream, for example. Large changes in syngas composition would also be intolerable.

A proposed scheme to satisfy these stipulations appears in Fig. 2-1. Downstream of the gasifier and gas intercooler, where the syngas has reached the specified temperature for Hg control, syngas enters a bed of Perovskites that uniformly releases O_2 into the process stream. In the figure, the upper bed is releasing O_2 into syngas while a lower bed is being regenerated with O_2 off-line. Once the syngas has reached the uniform target O_2 level, it enters a bed of MinPlus where it maintains sufficient O_2 to remove a specified percentage of the Hg in the syngas in the available transit time. The Perovskite bed may run hotter than the MinPlus bed to optimize the O_2 release rate for a specified bed transit time, whereas cooler operation entails an energy penalty.

A fixed bed of Perovskites is used to introduce O_2 into the stream because fixed beds offer the best potential to uniformly disperse O_2 throughout the entire syngas stream. The flux of O_2 from this bed can be controlled by the loading of Perovskites in an inert material, such as alumina or quartz; the operating temperature; and the particle size of bed materials. The extent of oxidation of the Perovskites in the regeneration cycle may also be used to regulate the O_2 flux, although maximizing the O_2 storage also maximizes the duration of each O_2 release cycle. The MinPlus is also implemented as a fixed bed to

maximize the specific surface area per unit bed volume, and to also maximize the external film transport coefficient. Provided that the bed temperature and O_2 level sustain rapid intrinsic sorption activity, a fixed bed of MinPlus sustains the maximum possible Hg sorption rate, which can be exploited to minimize the pressure drop. We therefore expect this configuration to achieve Hg removal rates that are orders of magnitude faster than those monitored in the bench-scale tests at U. Utah under this project, which evaluated dilute MinPlus suspensions in O_2/N_2 streams.

Details on the major stages of this process are discussed in succeeding sections.

2.1.1 BOC's CAR Process

The introduction of O_2 into the syngas stream utilizes BOC's Ceramic Autothermal Recovery (CAR) process (Acharya et al. 2005; Tamhankar et al. 2002). It has been under development for several years as a better means to elevate the O_2 level in recycled flue gas in oxyfuel combustion systems. CAR exploits the oxygen storage capacity of Perovskite minerals at elevated temperatures in a continuous process that cycles between two primary stages: O_2 generation and oxygen storage. Extruded Perovskites are used in both stages in fixed bed configurations. In the generation stage, an oxygen deficient stream is passed through the bed to remove the stored oxygen while, in the storage stage, air is passed through a depleted bed until it reaches its oxygen storage capacity.

The process operates continuously by simultaneously operating manifolds of beds in both stages. The stages are run in a counter-current flow configuration to maximize the O_2 concentration of the product stream; i.e., by having the greatest oxygen storage at the outlet of the O_2 generation bed, the O_2 concentration in the product stream will be maximized. Oxygen sorption in Perovskite beds is exothermic, while the generation stage is endothermic, so heat exchange between the O_2 and product streams may be used to meet most of the energy requirements. In the oxyfuel application, an air stream is used to regenerate the Perovskites, which must be "washed" with steam to remove N_2 in the particle pores before the next O_2 generation stage. But such washing will be unnecessary in gasifier cleaning systems due to the availability of O_2 on-site.

The very low target O_2 level in the MinPlus application compensates for the higher operating pressure so that the O_2 generation rate will be comparable to that in oxyfuel systems. Suppose that the recycled flue gas in an oxyfuel system initially has an O_2 level of 3 %, whereas the oxidizer stream into the furnace must contain 30 % O_2 . A CAR system would need to generate the equivalent of 40 % of the recycled flue gas as O_2

to achieve 30 % O₂ in the furnace oxidizer stream. In the gasification application, the target O₂ level is under 1 % but the pressure is 25 to 40 times greater than in the oxyfuel application. These two factors compensate for each other, and the O₂ generation capacity for the gasification and oxyfuel applications would be comparable; in fact, since there is less diluent in the gasification product stream, slightly less O₂ generation capacity would be required for the gasification application.

It is also possible to decouple the CAR process from the gas cleaning system by operating it with low pressure superheated steam from the steam cycle in an IGCC process instead of syngas. This approach produces a steam/O₂ stream from the O₂ generation bed that would need to be injected uniformly into the syngas stream upstream of the MinPlus bed, which is not easy to do. The additional steam in the syngas product would then increase the load on the downstream condenser.

Alternative O₂ generation technologies should also be considered. Direct injection of on-site O₂ into the syngas would almost certainly create locally flammable mixtures or reverse diffusion flames that would significantly degrade the syngas quality. Oxygen transport membranes (OTMs) would also be difficult, if not impossible, to use to uniformly disperse the O₂ throughout the syngas mixture. Currently, OTMs are also plagued by concerns about structural integrity and sealing under power generation conditions, and about large-scale implementation. We propose the CAR process because it appears to be the only means to generate O₂ and simultaneously and uniformly introduce it into a syngas stream to maintain very low O₂ concentrations. It also uses familiar components without exotic materials constraints, all of which have already been extensively field tested in pressure swing adsorption units. Detailed engineering and economic evaluations for the oxyfuel application of CAR are available (Acharya et al. 2005).

2.1.2 The MinPlus Fixed Bed

MinPlus sorbent is manufactured from paper-industry recycling materials. Its composition is 41 % CaCO₃; 29 % Al₂O₃•2SiO₂; 23 % CaO; and 7 % inert solids. It also contains 2 % MgO, 1 % TiO₂, and less than 1 % of Fe₂O₃, SO₃, K₂O, P₂O₅, and CuO. It has less than 0.1% Cl, Na₂O, BaO, MnO, and CrO₂. None of the available literature on MinPlus field tests give a particle diameter, but it is probably ground to tens of microns for suspension application. Larger particle sizes may be required for fixed bed applications, to maintain tolerable pressure drops.

Since the temperature of the proposed MinPlus bed is isothermal within the range

from 650 to 850°C, and since the bed area per unit volume will be very large, we analyze Hg sorption in terms of equilibrium adsorption isotherms. When the Hg sorption capacity increases for progressively hotter temperatures, the Freundlich isotherm applies, which is

$$q = \left(\frac{1}{K_{AD}} \right) \left[\rho_{GAS} y_{Hg}^{Eq} \right]^{\frac{1}{n_{AD}}} \quad 2.1a$$

where q is the sorption level of Hg on the sorbent, $\mu\text{g/g}$; ρ_{GAS} is the syngas gas density, y_{Hg}^{Eq} is the mass fraction of Hg vapor in equilibrium with the sorbed species; and K_{AD} and n_{AD} are adjustable parameters assigned to fit laboratory analytical data. For more complex temperature dependences, the Langmuir adsorption isotherm applies, which is

$$q = \frac{n_{AD} \rho_{GAS} y_{Hg}^{Eq}}{1 + K_{AD} \rho_{GAS} y_{Hg}^{Eq}} \quad 2.1b$$

Again, K_{AD} and n_{AD} are adjustable parameters assigned to fit laboratory analytical data.

The parameters in the adsorption isotherms are specified from standard lab-scale breakthrough tests. In the Freundlich isotherm, the exponent on the equilibrium Hg concentration is actually a temperature dependence, because saturated vapor pressures are functions of temperature only. In the Langmuir isotherm, the temperature-dependence is explicit in K_{AD} . In particular, the order in the Freundlich isotherm may be specified from the following rearrangement of the isotherms for two test cases with different inlet Hg concentrations:

$$n_{AD} = \frac{\ln \left[\frac{C_{Hg}(T_1)}{C_{Hg}(T_2)} \right]}{\ln \left[\frac{q_0(T_1)}{q_0(T_2)} \right]} \quad 2.2$$

where the subscripts on temperature denote different tests. Once n_{AD} has been assigned, K_{AD} can be evaluated from each of the reported sorption capacities, according to

$$\ln K_{AD} = \frac{\ln C_{Hg}}{n_{AD}} - \ln q_0 \quad 2.3$$

The parameter assignments from breakthrough curves are based on the assumption that the Hg adsorbed on the entire sorbent bed is in equilibrium with the inlet Hg concentration in the gas phase by the end of the test period. But in an actual MinPlus bed in a gas cleaning system, the level of adsorbed Hg will rise continuously throughout the bed, beginning from the inlet plane and moving deeper into the bed in time. The following analysis describes the Hg concentration on the sorbent and in the gas phase along the entire bed throughout a sorption cycle to assess mass transport limitations. If the model predicts that the sorbent and outlet Hg concentrations have reached their equilibrium limits within the duration of a cycle, then mass transport limitations did not undermine the application of equilibrium adsorption isotherms. Otherwise, the bed specifications should be modified to comply with the constraints imposed by the adsorption rates.

Adsorption is assumed to be limited by the rate at which Hg is transported from the free stream in the packed bed to the external surface of an individual sorbent particle. The process becomes rate limiting as the concentration of the diffusing species vanishes, and is appropriate for this system because the Hg concentrations of interest are so small. Internal pore diffusion effects on Hg are assumed to be negligible for minPlus, pending additional characterization on its pore size distribution.

The model is based on species conservation in the gas phase and on the sorbent. The exchange of Hg between these phases is based on film diffusion, as seen in the following equations:

$$\frac{\partial C}{\partial \tau} = -\frac{\partial C}{\partial x} - \frac{(1-\varepsilon)\rho_s R_M}{\varepsilon} (C - C^*) \quad 2.4$$

$$\frac{\partial q}{\partial \tau} = \frac{C_{Hg}^0 R_M}{q_0 (C_{Hg}^0)} (C - C^*) \quad 2.5$$

$$R_M = \frac{a_s k_M L}{V_0} \quad \text{where} \quad \frac{k_M \phi}{V_0} = 0.91 \text{Re}^{-0.51} Sc^{-0.667} \quad 2.6$$

In these equations, C is the Hg concentration at any position at a point in time normalized by the inlet value, C_{Hg}^0 ; q is the sorption capacity normalized by the value for the inlet Hg concentration; τ is the nondimensional time, tV_0/L where V_0 is superficial gas velocity and L is bed length; and x is the position in the sorbent bed normalized by L . The mass transfer rate is proportional to the deviation from the equilibrium Hg concentration, C^* ,

and the mass transfer coefficient, k_M . The transport coefficient is evaluated for packed beds in terms of the Reynolds and Schmidt numbers, the particle sphericity, ϕ , and V_0 . The bed voidage, ε , the sorbent bulk particle density, ρ_S , and the specific particle surface area, a_S , also appear. For beds of MinPlus and an inert diluent, the sorbent concentration in the bed can be related to the properties of the inert components and sorbent particles in the filter cake with a mass balance, which can be rearranged to yield the following definition:

$$C_b = y_{SORBENT} \rho_b = y_{SORBENT} (1 - \varepsilon_b) \langle \rho_P \rangle = \frac{y_{SORBENT} (1 - \varepsilon_b)}{\frac{1 - y_{SORBENT}}{\rho_{ASH}} + \frac{y_{SORBENT}}{\rho_{SORBENT}}} \quad 2.7$$

where ρ_{ASH} and $\rho_{SORBENT}$ are the bulk particle densities of the inert components and sorbent in the bed, respectively. The external surface-to-bed volume for just the sorbent particles in the bed is evaluated as

$$a_b = \frac{6C_b}{\rho_{SORBENT} d_{SORBENT}} \quad 2.8$$

This system of linear, first-order partial differential equations may be solved with a library routine based on the method of lines. Once the parameters in an adsorption isotherm have been assigned, the scaling factor, $q_0(C_{Hg}^0)$ can be evaluated, and the system of equations is fully specified.

Since we do not have Hg sorption capacities for MinPlus under pertinent conditions, we simply illustrate the sorption dynamics with a previous application involving a mixed bed of granulated activated carbon (GAC) in coal flyash. In these simulations, a_S was evaluated for the average particle diameter; ε was set to 0.30, because polydisperse particles pack tighter than monodisperse spheres; ϕ was set to 0.95; and ρ_S was set to 1.8 g/cm³. The sample diameter and length were estimated from the reported sample weights, particle density, and bed voidage, according to $V_{Sample} = M_{Sample}/(\rho_S(1 - \varepsilon))$. The lengths were then evaluated for the range of estimated bed diameters. The resulting pairs of bed diameters and lengths were as follows: (0.6 cm/4.21 cm); (0.8/2.37); (1.0/1.52); and (1.2/1.05). All simulations were based on an assumed bed diameter of 1 cm and a corresponding length of 1.52 cm.

The predicted effluent Hg concentrations and the local sorption capacities at the bed outlet appear in Fig. 2-2 versus the nondimensional time scale. On this time scale, the extent of the curves corresponds to a uniform test duration of 10 min. Since these are outlet conditions, when the gas concentration achieves its inlet value, the sorption

Figure 2-2. Outlet compositions (top) and sorption capacities (bottom) versus nondimensional time for GAC samples based on the Freundlich isotherm.

capacity is equilibrated with the inlet composition throughout the entire bed, and the nondimensional capacity equals unity. This condition is satisfied at 150°C, and nearly satisfied at 110°C, where the sorption capacity at the outlet is over 90 % of the equilibrium level. Since the outlet value is over 90 %, the average value over the entire bed is much closer to unity. But the case for 80°C is far from equilibrated. The sorption capacity at the outlet plane is under 60 %. In contrast to the equilibrium sorption capacity approaching 80 % for the entire bed, the estimated capacity is under 60 %. Apparently, mass transfer limitations prevent the equilibration of the entire bed during the available test time at the lowest test temperature.

To determine if uncertainties in the bed dimensions were responsible for the significant mass transfer limitations at the lowest temperature, cases were run for bed diameters from 0.6 to 1.6 cm, for which the bed length decreased from 4.2 to 0.6. Over this range, the outlet concentrations and sorption capacities were the same, reflecting compensation for the shorter residence times in longer beds by the higher mass transfer coefficients associated with the faster gas velocities.

For this example, we would therefore restrict this analysis to temperatures above 110°C, where the adsorption isotherm is appropriate. Analogous calculations for a mixed bed of MinPlus would determine whether or not mass transfer limitations were important, provided that data were available to specify the parameters in the adsorption isotherms.

2.2 The Lifetime of O₂ in Syngas

One crucial aspect of the proposed MinPlus implementation scheme is the lifetime of O₂ in the syngas stream as it moves from the CAR bed through the MinPlus bed. MinPlus is active for Hg sorption only if O₂ is present at some level near 0.4 %, although the precise threshold is unknown. We evaluated the decay in various O₂ concentrations from the CAR bed with an elementary reaction mechanism for the homogeneous conversion of O₂ in syngas mixtures from two popular entrained-flow gasifiers. Following the estimated syngas compositions from Shell and GEPS gasifiers in the next section, we review the detailed reaction mechanism before presenting the O₂ decay histories in a third subsection.

2.2.1 Syngas Compositions from Shell and GEPS Gasifiers

Two entrained-flow gasifier configurations were characterized for our analysis: The Shell gasifier and the GEPS a.k.a. Texaco gasifier. Gasifier manufacturers do not report detailed operating conditions. However, several independent analysts have reported

Table 2.1. Reported gasifier inlet conditions for various coal types.

Coal	C, daf wt. %	O ₂ /coal	H ₂ O/coal	H/C	O/C	Ref.
Shell Gasifier						
Zheng B	61.9	0.40	0.01	1.30	1.01	Zheng '05
Zheng C	73.2	0.73	0.02	0.81	1.12	Zheng '05
REI I6	78.2	0.84	-	0.83	0.94	Bockelie '03
Zheng A	79.0	0.90	0.09	1.00	1.14	Zheng '05
REI Dra3	82.6	0.93	-	0.86	1.09	Bockelie '03
REI Dra4	82.6	0.88	0.07	0.99	1.10	Bockelie '03
GEPS Gasifier						
Zheng B	61.9	0.64	0.54	2.75	2.10	Zheng '05
Zheng C	73.2	0.84	0.54	1.94	1.82	Zheng '05
Akun	77.3	0.92	0.51	1.88	1.58	Akunuri '99
REI SF3	78.8	0.87	0.65	2.03	1.65	Bockelie '03
Zheng A	79.0	0.97	0.54	1.86	1.64	Zheng '05
REI SF5	79.1	0.89	0.68	2.08	1.68	Bockelie '03
REI SF4	79.4	0.87	0.62	1.98	1.62	Bockelie '03
REI I6	78.2	0.90	0.58	1.89	1.54	Bockelie '03
REI Lem	82.5	0.89	0.59	1.90	1.61	Bockelie '03
REI P8	83.9	0.98	0.69	2.00	1.59	Bockelie '03

detailed gasifier simulations for gasifier test programs (Doering and Cremer 1995; Akunuri and Frey 1999; Bockelie et al. 2003; Zheng and Furimsky 2005). Here we use reported fuel properties, feedstream ratios, exit gas temperatures, and syngas compositions to specify universal temperature histories for the Shell and GEPS entrained-flow gasifiers. Based on the conditions reported for coals that have been tested at Buggenheim and Coolwater, we will also develop an estimation procedure to assign operating conditions for any coal in these two gasifiers.

The most variable operating conditions for both gasifiers are the O₂/coal and steam/coal ratios, because these ratios are the means to operate the gasifiers to produce essentially uniform syngas compositions from a broad range of fuel quality. The reported values for both gasifiers are collected in Table 2.1, along with the daf C-contents of the coal feeds and the atomic H/C and O/C ratios of the whole feedstreams. These later ratios are evaluated as

$$\frac{H}{C} = \left(\frac{12}{1} \right) \frac{\% H_{dry} + \frac{2}{18} \frac{steam}{coal}}{\% C_{dry}} \quad 2.9$$

$$\frac{O}{C} = \left(\frac{12}{16} \right) \frac{\% O_{dry} + \frac{O_2}{coal} + \frac{16}{18} \frac{steam}{coal}}{\% C_{dry}} \quad 2.10$$

where the C-, H-, and O-contents are on a dry basis, and the coal feedrate is for dry coal, so that the steam/coal ratio also accounts for inherent coal moisture. All the hydrogen and oxygen in steam are assumed to participate in syngas reforming, due to the very high operating temperatures.

In Table 2.1, the coals under each gasifier type are arranged in descending order of increasing rank. Shell gasifiers are operated with dry coal feeds, and little or no steam is injected downstream. Consequently, the O₂/coal ratio is adjusted to regulate the H/C and O/C ratios for syngas reforming. This ratio is generally increased for coals of progressively greater rank to maintain H/C ratios from 0.80 to 1.00 and O/C ratios from 0.90 to 1.15. Only the H/C ratio for the very low rank lignite sample (Zheng B) is outside these ranges. GEPS gasifiers are fed with coal slurry that has 65 wt. % coal, so steam/coal ratios fall between 0.50 and 0.70. The O₂/coal ratios are generally increased for coals of progressively higher rank although, as for Shell gasifiers, the variation in this parameter for coals with C-contents over 77 % is minimal. For all but the lowest rank coals, the H/C was varied from 1.85 to 2.10 and O/C varied only from 1.54 to 1.65.

The feed PSD was reported to have a mean size of 40 μm for both gasifiers (Zheng and Furimsky 2005). This value is plausible for the Shell gasifier, and will be used in our calculations. But it is too small for the slurry fed to the GEPS gasifier. We will use the PSD obtained from METSo for typical gasifier feed slurries in our calculations.

The only information on the thermal history we found were the exit gas temperatures calculated by Bockelie et al. (2003) for various cases in the Shell and GEPS gasifiers. We assumed the temperature histories in Fig. 2-3 for both gases and radiation temperature for these gasifier types in our calculations, with nominal residence times of 2.0 and 2.8 s for the Shell and GEPS gasifiers, respectively. Only the exit gas temperatures were changed to the calculated values for the different cases; to maintain uniform total residence times for each gasifier type, the times at the maximum temperature were adjusted to compensate for the variable times to reach the different exit gas temperatures (at the assumed uniform gas quench rate). This procedure worked well for all cases except REI Lem, whose exit gas temperature of only 940°C was too low for equilibrium gas compositions to apply. For this case only, the exit temperature was

Figure 2-2. Estimated thermal histories for (Solid curve) Shell and (Dashed curve) GEPS gasifiers.

assigned as 1050°C, which gave the correct syngas composition. The GEPS gasifier operated at 4.1 MPa for all cases, and the Shell gasifier was operated from 2.0 to 2.7 MPa.

The operating conditions and coal properties were entered into PC Coal Lab[®], which is NEA's kinetics software for any coal at any operating conditions, to simulate several cases that were reported with measured syngas compositions. The simulations were run in the mode that accepts O₂/coal, steam/coal, CO₂/coal, and N₂/coal ratios as input, and one of the user-specified thermal histories in Fig. 2-3 for each case. This mode also accepts the extents of oxidation of char and soot prior to the gasification simulations, which were estimated to be 30 and 40 daf wt. %, respectively, for the Shell gasifier, and 35 and 45 wt. % for the GEPS gasifier. The greater extents of oxidation in the GEPS gasifier reflect the much greater O/C ratios. Also, these values are reasonably consistent with simulations that used detailed finite-rate kinetics for gas phase oxidation chemistry and CBK/E for char and soot oxidation for similar operating conditions.

The predicted syngas compositions for the available cases with reported syngas compositions are collected in Table 2.2. All values listed as "Measured" were taken from field tests, except those labeled as "Zheng A," which were specified in process

Table 2.2. Evaluation of predicted syngas compositions, dry vol. %.

Test	CO		H ₂		CO ₂	
	Meas.	Pred.	Meas.	Pred.	Meas.	Pred.
Shell Gasifier						
REI I6	62.7	62.2	25.5	24.1	2.2	2.5
Zheng A	62.9	64.6	28.3	25.2	2.3	3.8
REI Dra3	65.3	67.0	26.2	24.6	1.6	2.1
REI Dra4	63.4	64.2	28.4	28.0	1.5	2.3
GEPS Gasifier						
REI SF3	43.0	42.8	38.1	36.3	18.1	18.8
Zheng A	46.5	52.1	34.6	30.0	15.3	15.9
REI I6	44.9	51.1	38.5	34.1	15.5	12.9
REI Lem	44.2	44.0	36.9	34.1	18.0	18.7
REI P8	44.3	50.2	39.4	35.0	15.5	13.3

Table 2.3. Predicted compositions of whole syngas, vol. %.

Test	CO	H ₂	CO ₂	H ₂ O
Shell Gasifier				
REI I6	60.7	23.5	2.4	2.5
Zheng A	61.0	23.8	3.6	5.5
REI Dra3	65.5	24.0	2.0	2.3
REI Dra4	62.1	27.0	2.2	3.3
GEPS Gasifier				
REI SF3	32.6	27.6	14.3	23.9
Zheng A	40.3	23.2	12.3	22.6
REI I6	40.3	26.9	12.3	22.6
REI Lem	34.7	26.9	14.7	21.2
REI P8	38.9	27.1	10.3	22.5

simulations with AspenPLUS (Zheng and Furimsky 2005). All syngas compositions are reported on a moisture-free basis, in mole %. All predictions for the Shell gasifier are within measurement uncertainties and, although the discrepancies are greater for the GEPS products, the predictions are as accurate as they need to be for this phase of the project. The compositions in Table 2.2 do not sum to unity due to the omission of N₂ and other minor species, such as CH₄, H₂S, COS, etc. The whole syngas compositions for the same tests appear in Table 2.3.

The representative mixtures selected for the O₂ decay calculations are labeled as

“REI-Dra4” for Shell and as “REI-I6” for GEPS in Table 2.3, because these syngas compositions are intermediate values for these series. Since the compositions are so similar for all these cases, it is not necessary to examine how variations in the major species concentrations would affect the O₂ decay histories.

2.2.2 Syngas Reforming Chemistry

The major gaseous species in the syngas are CO, CO₂, H₂O, H₂, CH₄, C₂- and C₃-hydrocarbons, oils, and PAH. C₂-hydrocarbons consist mainly of ethane and ethylene, and C₃-hydrocarbons consist mainly of propylene. Oils are mixtures of BTX and PCX. A suitable reaction mechanism for such mixtures must remain accurate for the large variations in composition associated with different coal types, and also with a fairly broad range of S. R. for rich mixtures, and of variable steam/coal ratios. Of course, the mechanism must be accurate for moderate temperatures at pressures from 2 to 9 MPa.

NEA’s gas phase reaction mechanism was assembled from components of various mechanisms developed for diesel combustion applications. The base mechanism comprising 316 reactions among 66 species, including hydrocarbons up to C₃, was obtained from the reduced mechanism for n-heptane developed by Seiser et al. (2000). This mechanism has the distinct advantage of being developed from a parent mechanism (Curran et al. 1998) that was validated for pressures from 0.1 to 4.2 MPa; temperatures from 280 to 1430°C, and equivalence ratios from 0.3 to 1.5. Its only disadvantage was that the base mechanism explicitly specified the rate constants for reverse reactions, which prevented a smooth approach of predicted gas compositions to their equilibrium compositions for long reaction times. To restore this important feature, we instead calculated the reverse rate constants from equilibrium constants. When the reconstructed mechanism was evaluated for its relaxation to equilibrium compositions, we adjusted the rate constants within reasonable limits except, perhaps, for CH₃+HO₂; C₂H₃+O₂; H+O₂; and CO+OH. In addition, the reaction submechanism for H₂ and CO was updated based on a recent study (Davis et al. 2005).

Then a reaction submechanism for oils consisting of benzene, toluene, and phenol (Pitz et al. 2003) was added to the base mechanism, increasing the size to 566 reactions among 154 species. Since the oils from coal tar decomposition are mixtures of BTX and PCX, they have to be expressed as equivalent amounts of benzene, toluene, and phenol in the simulations, according to the following conversion relations: In the tar conversion mechanism, the composition of oils is uniform for all coals, at 13.7 mole % C₆H₆; 17.5 % C₇H₈; 15.5 % C₈H₁₀; 28.5 % C₆H₆O; 15.5 % C₇H₈O; and 9.3 % C₈H₁₀O, which implies a

molecular weight of 96.7 g/mole. The percentages were assigned from measured yields of these hydrocarbons from a very broad range of coal quality (Xu and Tomita 1987). This mixture is then expressed in terms of equivalent amounts of benzene, toluene, and phenol with the following relation:

$$W_i = n_{oil} x_j MW_j \quad 2.11$$

where W_i is the equivalent weight of component i per kg of oil; n_{oil} is the moles of oil per kg; x_j is the mole fraction of component j in the original oil mixture; and MW_j is the molecular weight of component j . These relations are evaluated by equating (1) the moles of C_6H_6 in the original oil to the moles in the gas phase; (2) the moles of $C_7H_8 + C_8H_{10}$ to the moles of gaseous C_7H_8 ; and (3) the moles of $C_6H_6O + C_7H_8O + C_8H_{10}O$ to the moles of gaseous C_6H_6O .

Chemistry for neither N-species nor S-species was within the scope of the current project, but it could be included in future work.

2.2.3 Evaluation of O₂ Decay Histories

The results in this section determine the dynamic consumption of O₂ in syngas across 2 s isothermal stage, presumably when the process stream is passing through the MinPlus bed. The goal is to determine the length of time that O₂ levels are likely to be high enough to sustain adequate MinPlus activity for Hg sorption for different bed temperatures, syngas compositions, and initial O₂ levels. These calculations were prepared in three distinct stages: (1) A quench stage in which syngas is cooled from the temperature at the gasifier outlet to the MinPlus bed temperature; (2) A rapid O₂ injection and mixing stage, in which a specified O₂ injection is rapidly mixed with the syngas stream; and (3) The O₂ decay stage, when O₂ reacts homogeneously with syngas until it is either eliminated or reaches a saturation limit.

The quench stage converts the crude four-component syngas compositions for the gasifier outlets in Table 3.3 to whole syngas compositions, including radical species. It starts at 1200°C with 62.1 % CO; 27 % H₂; 2.2 % CO₂; and 3.3 % H₂O for the Shell gasifier, and at 1050°C with 40.3 % CO; 26.9 % H₂; 12.3 % CO₂; and 22.6 % H₂O for the GEPS gasifier. The syngas quench rates are 525 and 1100°C/s for the Shell and GEPS gasifiers, respectively, based on the estimated thermal histories in Fig. 2-2. As MinPlus bed temperatures are changed from 600 to 1000°C in the simulations, the durations of the quench stages were increased. The quench period was represented by a series of continuously stirred tank reactors (CSTRs) with uniform mean residence times assigned

as the time to change the stream temperature by 100°C at the specified quench rate. From 1 to 6 CSTRs were used to depict the quench stages among the cases in this study.

According to the proposed MinPlus application process, O₂ is introduced into the syngas as it is released from Perovskite particles in a CAR bed. But in the simulations, the entire O₂ stream is perfectly mixed into the syngas stream in 1 ms at the operating temperature of the succeeding isothermal stage. Our intent is to generate a uniform O₂ level in the syngas stream that provides a well-defined initial condition for the subsequent O₂ decay calculations. This ideal situation was achieved in cases with isothermal temperatures of 600 and 700°C. But appreciable amounts of O₂ decomposed during the 1 ms mixing period at hotter temperatures, and almost half the injected O₂ was eliminated in the mixing tank at 1000°C.

The O₂ decay histories were evaluated in a series of four CSTRs operated isothermally at temperatures from 600 to 1000°C. Each CSTR had a mean residence time of 0.5 s, for a total duration of the O₂ decay period of 2 s. NEA's syngas reforming mechanism was initialized with the whole syngas composition out of the mixing tank, and evaluated to assign outlet gas compositions from each of the four CSTRs. Note that only homogeneous chemistry was used to determine the O₂ decay histories. Heterogeneous chemistry was omitted from our calculations, both along the CAR bed and along the MinPlus bed, because rates on these potentially catalytic materials are unknown. Whereas the contribution from heterogeneous chemistry on MinPlus is expected to be negligible, Perovskites are used for CH₄ activation, albeit under oxidizing rather than reducing conditions.

The baseline O₂ decay histories for both gasifiers appear in Fig. 2-3. Note the different breaks in the scales for the O₂ axis in both panels. All these cases are based on an O₂ injection rate of 1 % of the syngas streams, while the temperatures of the O₂ decay stages were varied from 600 to 1000°C. With a syngas composition from a Shell gasifier, the O₂ levels change in a simple exponential decay at faster rates for progressively hotter temperatures. After 0.5 s only 130 ppm O₂ remains at 1000°C but 300 ppm remains at 700°C and 2000 ppm remains at 600°C. After 1 s, there is only 200 ppm at 600°C and less than 20 ppm at all other temperatures. Thereafter, all the O₂ levels are in the single-digit ppm-range. For the syngas composition and pressure in the Shell gasifier, the MinPlus bed should be operated no hotter than 700°C with a residence time no longer than 0.5 s.

With the syngas composition from a GEPS gasifier, the O₂ decay characteristics

Figure 2-3. Predicted O₂ decay histories for (upper) Shell and (lower) GEPS gasifiers at various temperatures for the baseline O₂ injection rate of 1 % of the syngas streams.

are the same for temperatures of 800°C and hotter, but qualitatively different for 600 and 700°C. For both these temperatures, the O₂ level reaches a stable saturation limit that persists throughout the entire 2 s isothermal decay period in the simulations. The limiting levels are 70 ppm for 600°C and 170 ppm for 700°C. So for extended residence times up to 2 s in the MinPlus bed, it would be better to operate the bed at 700°C than at 600°C, although we do not yet know if MinPlus would remain active for Hg sorption under 170 ppm O₂ in syngas. For residence times of 0.5 s, however, 920 ppm O₂ would persist at the outlet of a 600°C bed vs. only 145 ppm from a 700°C bed.

We did not identify a mechanistic basis for the saturation limits for O₂ in the GEPS syngas, but did determine that it is associated with the higher pressure of the GEPS gasifier, rather than with its syngas composition. When the two gasifier pressures were exchanged for the two syngas compositions, the case for the Shell gas composition at 41 atm exhibited an O₂ saturation limit of 153 ppm whereas that for the GEPS composition at 23.5 atm had fallen to only 30 ppm. We suspect that these saturation limits reflect a delicate balance determined by the size of the oxyhydroxyl radical pool, which is a sensitive function of both temperature and pressure. Whether they are real or simply artifacts of obscure parameter assignments in the syngas reforming mechanism is difficult to establish, especially since this mechanism was not directly validated for stoichiometries as rich as the ones in these calculations. Bear in mind that radical pools would almost certainly be affected by Perovskite and MinPlus surfaces via heterogeneous recombination reactions, and such chemistry was not included here. For the time being, we will emphasize the potential existence of stable O₂ levels in syngas for as long as a few seconds at the highest gasifier pressures, noting that the operating conditions that form them are still subject to large uncertainties.

The impact of O₂ injection on syngas quality is seen in the product compositions after the simulated MinPlus bed in Table 2.4. Even though the reductions in CO become greater for progressively hotter operating temperatures, the levels of H₂ actually increase (primarily due to changes in total moles); actually, none of these changes are very significant because so little O₂ is added to the syngas.

The results in Fig. 2-4 characterize variations in the O₂ injection rate from 0.5 to 4 times the baseline value of 1 % of the syngas flow. For the Shell syngas composition, the O₂ levels increase for progressively greater injection rates across the entire time domain. In this situation, the O₂ injection rate would be specified from the adverse impact on syngas quality. With the GEPS syngas composition, there is a transition from the stable O₂ saturation limit for injection rates as great as the baseline rate to O₂ decay histories

Table 2.4. Syngas compositions after 2 s of O₂ decomposition.

Gasifier	T, °C	CO, %	CO ₂ , %	H ₂ O, %	H ₂ , %
Shell	600	60.9	3.36	3.39	26.9
	700	60.9	3.34	3.39	26.9
	800	60.8	3.46	3.30	27.0
	900	60.7	3.65	3.10	27.2
	1000	60.6	3.74	3.03	27.3
GEPS	600	39.3	13.3	20.7	26.7
	700	39.2	13.4	20.6	26.8
	800	38.3	14.3	19.8	27.6
	900	38.3	14.3	19.8	27.6
	1000	37.7	14.9	19.2	28.2

that decay continuously for greater injection rates. Without the saturation limit, O₂ levels increase for progressively greater injection rates across the entire time domain, albeit by very little. The sensitivity to injection rate is much greater for cases with a saturation limit, although it appears that the baseline rate is close to the optimal value that maximizes the ultimate O₂ level.

2.3 Summary Recommendations for MinPlus Applications With Syngas

NEA's proposed process for MinPlus applications to remove Hg from syngas streams appears to be feasible, pending further assessments of additional technical issues. The operating temperature window for Hg capture with this sorbent is from 650 to 850°C, due to phase transformations that inhibit Hg sorption out of this range. The scheme utilizes the CAR process to uniformly introduce sufficient O₂ to maintain MinPlus's Hg sorption activity under highly reducing conditions. Most important, we found that the O₂ lifetimes for syngas from Shell and GEPS gasifiers provided sufficient time for Hg sorption on MinPlus. For Shell gasifier conditions, up to 0.5 s was available for Hg sorption for temperatures up to 700°C. And for the very high operating pressure of GEPS gasifiers, the O₂ levels reached a stable saturation limit that persisted for at least 2 s provided that the temperature was no hotter than 700°C. The limit was 170 ppm O₂ at 700°C but only 70 ppm at 600°C. Changing the O₂ injection rate off the baseline value of 1 % of the syngas stream did not elevate these saturation limits. Adverse impacts of O₂ injection on syngas quality were minimal, because the O₂ injection rates were so small; whereas the CO mole fractions diminished slightly the H₂ mole fractions increased for most conditions.

Figure 2-4. Predicted O_2 decay histories for (upper) Shell and (lower) GEPS gasifiers for various O_2 injection rates referenced to 1 % of the syngas flow for the baseline case.

Due to limitations of schedule and budget, several important technical issues could not be properly evaluated at this stage, including the following:

- The O₂ level needed to maintain Minplus's Hg sorption activity was found to be no greater than 0.4 % at atmospheric pressure under O₂/N₂ mixtures. To maintain the same O₂ partial pressure, this threshold could be reduced to 170 ppm at 23.5 atm and 100 ppm at 41 atm, which are the respective operating pressures of Shell and GEPS gasifiers. This threshold needs to be better quantified. We also need to know if syngas components affect the Hg sorption activity of MinPlus, or if MinPlus sustains heterogeneous chemistry with syngas components.
- Since the O₂ levels needed to sustain MinPlus's Hg sorption activity are comparable to the O₂ saturation limits for GEPS gasifier conditions, the existence of these limits should be verified in tests. We also need to verify that elevated pressures are essential to their existence, as evident in our model calculations.
- The CAR process to generate O₂ from Perovskite minerals is already developed for oxyfuel applications. We found that slightly lower O₂ generation rates would be needed for the MinPlus application than those involving oxyfuel. However, a major uncertainty is whether or not syngas components will react heterogeneously with oxidized Perovskites under MinPlus operating conditions. It also remains to be demonstrated that Perovskites may be regenerated with O₂ under hot gas cleaning conditions without steam washing.
- Test data from U. Utah indicated that Hg sorption activities for MinPlus at 700°C were in the same range as the maximum activity at 900°C. In addition, both equilibrium Hg adsorption capacities and intrinsic sorption kinetics need to be monitored for temperatures from 600 to 750°C at elevated pressures to provide the rate data needed to design a fixed bed of MinPlus.

3.0 SCALING DEMONSTRATION

Originally, results from the lab-scale Hg sorption tests at U. Utah were supposed to be analyzed to validate a reaction mechanism, then that mechanism was to be used to extrapolate the sorbent performance for selected warm gas cleaning systems. But once NEA's objectives were shifted away from the kinetic analysis toward the issue of O₂ decay in syngas streams, we were no longer in a position to demonstrate an extrapolation to gasifier cleaning systems. Instead, this chapter demonstrates satisfactory extrapolations of the sorbent performance from a bench-scale test under oxidizing conditions to the performance in a pilot-scale coal-fired furnace.

First, we review the available data, then describe NEA's proposed sorption mechanisms for MinPlus, and ultimately validate the predictions for the pilot-scale flame with the available data.

3.1 MinPlus Database for Oxidizing Flue Gas

Two sets of experimental data are available on Hg sorption on MinPlus: (1) Bench-scale Hg sorption data from a fixed bed of MinPlus at various temperatures under an inert atmosphere; and (2) Measured Hg removals across a fabric filter (FF) during coal combustion in a pilot-scale furnace. Biermann et al. (2003) described the tests in detail, so only the required items for our simulations are reported here.

3.1.1 Lab-Scale Hg Sorption Tests

Fixed bed experiments were performed at U. Arizona. A stream of N₂ doped with 125 ppb Hg⁰ was passed through a temperature-controlled packed bed of 60 g of MinPlus. Mercury concentrations at the inlet and outlet of the reactor were measured by a Buck photo-analyzer. Any Hg²⁺ in the sampling line was converted to Hg⁰ by reaction with stannous chloride solution upstream of the detector. Hg sorption levels for various temperatures appear in Fig. 3-1. Hg sorption is less than 20 % at the lower temperatures but, above 400 °C, increases rapidly for progressively hotter temperatures. The highest temperature measured was slightly below 600 °C where Hg sorption was about 75 %. Thermogravimetric analysis showed that Hg begins to desorb from MinPlus at temperatures above 900 °C, presumably when the sorbent is converted into mullite and gehlenite and loses its internal surface area.

3.1.2 Pilot-Scale Hg Sorption Tests

MinPlus was also evaluated in Southern Research Institute's (SRI) 1.0 MW

Figure 3-1. Measured temperature dependence of Hg sorption in a fixed bed of MinPlus.

Combustion Research Facility (CRF). The system was fired with Choctaw bituminous coal whose properties appear in Table 3.1. The primary furnace operating conditions are described in Table 3.2, and are representative of flue gas from full-scale power plants in every respect. Biermann et al. (2003) reported a measured temperature history for flue gas from the furnace exit to the FF which is reproduced in Fig. 3-2. It can be resolved into two distinct quench stages, the first of which agrees well with published data for full-scale gas cleaning systems. After the flue gas was quenched in a series of heat exchangers, it passed through a FF operated at 160°C. MinPlus was injected in the upstream duct at approximately 850°C in a compressed air carrier gas. The carrier gas flowrate was approximately 3 % of the total flue gas flowrate. The transit time of MinPlus sorbent to the inlet of the FF was approximately 4.4 s. Mercury levels were detected before and after the FF with a PS Analytical stack gas analyzer, and sample gases were withdrawn using a QSYS probe from Apogee Scientific to eliminate additional Hg oxidation on filtered flyash and unburned carbon (UBC).

In a baseline test, the total Hg inventory was estimated from the coal-Hg content to be 5.4 $\mu\text{g}/\text{nm}^3$, which is slightly lower than the measured Hg vapor level of 6.0 $\mu\text{g}/\text{nm}^3$ at the FF inlet. This discrepancy is actually smaller than it is in most tests, and was taken

Table 3.1. Choctaw Bituminous Coal Analyses.

Proximate Analysis, as rec'd wt. %	
Moisture	2.0
Ash	4.2
Volatiles	31.8
Proximate Analysis, daf wt. %	
Carbon	85.4
Hydrogen	5.2
Nitrogen	2.0
Sulfur	1.0
Oxygen	6.5
Chlorine	0.01
Hg, ppmw	0.08
Calorific Value, Btu/lb	14019

Table 3.2. CRF Operating Conditions.

Coal feed rate, lb/hr	259
Air feed rate, SCFM	751
Furnace exit O ₂ level, %	3.9
Flue Gas Composition at FF inlet	
O ₂ , %	6.8
CO ₂ , %	12.8
CO, ppm	82
NO _x , ppm	251
SO ₂ , ppm	475

as an indication that no particulate-bound Hg (Hg-P) formed via inherent sorption on UBC and, perhaps, other flyash components. The best data to evaluate MinPlus was obtained with a sorbent injection rate of 22 lb/hr. Mercury speciation as fractions of the total Hg inventory across the FF with and without MinPlus appear in Fig. 3-3. These results are based on a total Hg inventory of 6 $\mu\text{g}/\text{nm}^3$, which is the sum of the measured baseline speciation. Without MinPlus, half the total Hg is oxidized on UBC by the time it reaches the FF inlet. The FF removes just over 40 % of the Hg but does not alter the comparable proportions of Hg⁰ and Hg²⁺ vapors very much. With MinPlus, almost 50 %

Figure 3-2. Measured temperature history of flue gas in the CRF from the furnace exit to the FF inlet.

Figure 3-3. Hg speciation across the FF with and without MinPlus as percentages of the total Hg inventory.

of the Hg inventory is present as Hg-P at the FF inlet. The FF removes an additional 30 % so that only 20 % of the inventory is emitted. Again, the proportions of Hg^0 and Hg^{2+} vapors are the same in the emitted flue gas. In summary, MinPlus injection removes an additional 40 % of the Hg inventory over and above the inherent removal level.

Lower MinPlus injection rates were also tested but these data were affected by sorbent deposits in cracks in the duct. These deposits continued to remove Hg and thereby distorted the true relation between Hg removal and MinPlus injection rate. So this data will not be included in our validation work.

3.2 Mechanisms for Hg Sorption on MinPlus

NEA's approach to predicting Hg speciation is distinctive for its reliance on detailed reaction mechanisms, rather than statistical correlations and simple scaling laws. Two separate mechanisms were developed to simulate the test data discussed in the previous section. One describes Hg sorption on MinPlus sorbent, both in fixed beds and in suspension, and the other describes Hg oxidation and sorption on suspended UBC particles. These mechanisms are described separately in two succeeding sections.

3.2.1 Reaction Mechanism for Hg Sorption on MinPlus

The reaction mechanism for Hg sorption on MinPlus resolves finite-rate adsorption and desorption from the sorbent, based on the following two steps for chemisorption of gaseous Hg with surface sites on the sorbent:

where StSA(s) and StHg(s) denote unoccupied and Hg-P sites, respectively. Mercury vapors are adsorbed on unoccupied sites by reaction 1, then desorb back into the gas phase via reaction 2. Dynamic rate equations for the surface coverages describe the accumulation on clean surfaces to an ultimate sorption capacity. The ultimate capacity will equal the equilibrium sorption capacity only if the kinetics reach their equilibrium rates. But no equilibrium adsorption isotherms are postulated or incorporated into the mechanism.

In this mechanism, no distinction is made between the Hg^0 and Hg^{2+} vapors for

the adsorption and desorption steps. This assumption is sufficient to describe the Hg sorption in the MinPlus packed bed experiments (cf. Fig. 3-1) because only Hg^0 was present in the test mixture. Moreover, as seen in Fig. 3-3, MinPlus does not affect the Hg speciation in the vapor phase and, therefore, there is no need to distinguish the forms of Hg vapor in the sorption mechanism. We note that the calculations presented in the annual report by Blowers et al. (2005) suggests that HgCl_2 has a greater adsorption energy than Hg^0 , but we would need additional Hg speciation data to translate this difference into distinctive sorption rates for the two forms of Hg.

3.2.2 Reaction Mechanisms for Hg Oxidation and Sorption on Unburned Carbon

Mercury continuously oxidizes on UBC particles as the flue gas is quenched from the furnace exit temperature as it moves through the superheater, economizer, and air preheater. Further downstream the major product of this chemistry shifts from Hg^{2+} vapor to Hg-P, due to a shift in the rate limiting step from adsorption to desorption control. NEA's complete mechanism for UBC particles is a hybrid homogeneous and heterogeneous reaction mechanism for in-flight Hg oxidation and sorption on UBC while whole flue gas moves through the gas cleaning system. The basic framework of the mechanism was reported by Niksa and Fujiwara (2003). Later, Niksa and Fujiwara (2004) updated this mechanism to incorporate Hg sorption on UBC as well as oxidation. The mechanism had been validated using field-test data on inherent Hg control from 24 full-scale power plants that represent 35 gas cleaning configurations (Krishnakumar, Naik, and Niksa 2006). This comprehensive mechanism is used for modeling the in-flight oxidation and sorption on UBC in this work. It includes the following reactions:

where StSA(s), StCl(s), and StHgCl(s) denote unoccupied, chlorinated, and Hg-P sites on UBC, respectively. Equations 3.3 and 3.4 are for chlorination and regeneration of UBC surface sites and Eq. 3.5 is for reverse chlorination in the presence of moisture; Eqs. 3.6

and 3.7 are for Hg^0 oxidation and subsequent desorption of HgCl ; and Eq. 3.8 is for HgCl_2 adsorption on unoccupied sites.

In brief, mercury transformations occur while flue gases are cooled along a gas cleaning system. At the furnace exit, only Hg^0 is present and the UBC is oxidized but otherwise clean. The process begins when temperatures are cooled into the range where HCl in the flue gas chlorinates some of the carbon sites in a reversible reaction. With further cooling, Hg^0 adsorbs at appreciable rates onto the chlorinated sites. Since desorption remains relatively fast, an HgCl intermediate rapidly desorbs into the gas phase, where it oxidizes into HgCl_2 provided that sufficient gaseous Cl_2 is available. In this temperature range, there is little sorption but extensive oxidation. As the particles are cooled further, the desorption rate becomes controlling, which implies that surface coverage increases, ultimately, to the equilibrium sorption capacity. There is little additional oxidation in the low temperature range, because the HgCl cannot leave the carbon surface. And HgCl on the carbon surface constitutes sorbed or “particulate” Hg . A reverse adsorption step for HgCl_2 into adsorbed- HgCl is also included to depict the different sorption rates of Hg^0 and Hg^{2+} . Dynamic rate equations for the surface coverages describe the accumulation on clean surfaces to an ultimate sorption capacity. The ultimate capacity will equal the equilibrium sorption capacity only if the kinetics reach their equilibrium rates. But no equilibrium adsorption isotherms are postulated or incorporated into the mechanism.

3.2.3 Adjustments to Parameters in the Reaction Mechanisms

Rate parameters for the combined homogeneous/heterogeneous mechanism for Hg oxidation and sorption on UBC particles were obtained from Krishnakumar, Naik, and Niksa (2006). These parameters depend only on the coal rank and furnace operating conditions, particularly the LOI levels. None of these parameters were adjusted in the simulations reported in this chapter.

On the other hand, rate parameters for Hg sorption on MinPlus (associated with Eqs. 3.1 and 3.2) were adjusted to accurately describe both lab- and pilot-scale datasets. Both reactions have rate constants of Arrhenius form with a frequency factor and activation energy that must be specified. Only one set of these rate parameters is used for all simulations of MinPlus performance in this report.

3.3 Interpreting the Bench-Scale Experiments

The two distinct reaction mechanisms simulate Hg transformations continuously

along the packed bed of MinPlus as well as in the CRF tests from the furnace exit to the stack. No statistical database of Hg speciation measurements or gas cleaning conditions is involved at any point in our analyses. Each test is regarded as a distinctive event whose Hg transformations are determined by the operating conditions and fuel properties in that particular test, because that is the only means to achieve the highest accuracy. This section describes how the reaction mechanisms were used to interpret the bench-scale data; an extrapolation for the pilot-scale tests is in the following section, below.

The bench-scale experiments isolated the sorption of Hg^0 vapor onto the packed bed of MinPlus. The vapor phase contained only Hg^0 in N_2 , an inert carrier gas. Therefore, this system may be interpreted without any gas phase chemistry in the analysis. We developed a simple plug flow reactor model for the packed bed that imposes the Hg sorption mechanism described by Eqs. 3.1 and 3.2. This analysis also invokes an analogy to Hg sorption and oxidation in an accumulating filtercake on a FF. NEA's previous detailed analysis of the accumulating filtercake showed that Hg oxidation and sorption is confined to a very thin layer on the outer surface of the filtercake, due to the very high surface area per unit volume in this configuration. All gradients were confined to the layer, so that the gas and filtercake in the downstream section had uniform Hg speciation that is determined by adsorption equilibrium (which does not imply complete removal of Hg). In other words, the Hg speciation reaches an adsorption equilibrium with the filtercake determined by the speciation at the outer surface of the cake, temperature, and various filtercake characteristics.

Based on this analogy, we analysed the sorption of Hg on the packed MinPlus bed with an adsorption equilibrium analysis. Since equilibrium compositions are independent of the means to achieve them, we simulated the packed bed by running the normal plug flow calculations with finite-rate kinetics for times that were long enough to essentially achieve the equilibrium Hg sorption level. Typically, this approach takes 20 to 25 s of contact time in the simulations, and delivers reliable predictions for the packed bed performance. A similar methodology was used to simulate Hg transformations in the FF in the CRF as well.

All experiments were simulated for isothermal MinPlus beds. The results for 500°C are shown in Fig. 3-4. We see that all Hg^0 is slowly depleted as it is adsorbed onto the sorbent as Hg-P. For reaction times longer than 20 s, it approaches adsorption equilibrium where the Hg levels in the gas phase and on the sorbent do not change significantly. At 500°C, the equilibrium level of Hg-P is predicted to be 45 % of the Hg inventory.

Figure 3-4. Simulated Hg speciation for long reaction times in a packed bed of MinPlus at 500 °C.

Figure 3-5 compares the simulated Hg sorption removals in the packed bed at various temperatures to the measured values. The analysis does not predict the sorption of about 7 to 16 % Hg at temperatures below 400°C. Biermann et al. (2003) attributed this stage to physical adsorption, which we deliberately omitted because it makes a negligible contribution for the much hotter temperatures of interest in practical applications. Toward this end, our analysis accurately predicts the sharp increase in Hg sorption above 400°C with saturation to much slower sorption rates at temperatures greater than 550°C. This turnover is not evident in the data, which increases continuously through 580°C, the hottest temperature in the lab study.

Overall, the assigned kinetics for Hg sorption at various temperatures are in reasonably good agreement with the data. The increase in Hg sorption at higher temperatures is especially well represented by the model. Additional data for temperatures above 600°C will be helpful to rectify the differences between the data and predictions in this range.

Figure 3-5. Evaluation of the temperature dependence of Hg sorption for a packed bed of MinPlus, where data symbols denote measurements and the curve denotes calculations.

3.4 Extrapolations for the Pilot-Scale Tests

A similar plug flow model was also used to simulate the gas cleaning system from the furnace exhaust to stack in the tests at SRI. The primary difference is that the Hg/Cl chemistry was included as well as Hg sorption on MinPlus. NEA's Hg transformation mechanisms describe the dynamics of the essential reaction species as the flue gas moves from a furnace exit through the back-end heat exchangers and various APCDs, and into the stack. This approach necessarily requires more input information than static models, so why adopt it? The answer is simple: Static models fail to depict the primary parametric dependences on Hg transformations, as has been demonstrated several times by various groups. The main reason is that Hg transformations are governed by chemical kinetics and, with only a few exceptions, do not adhere to equilibrium constraints.

3.4.1 Detailed Test Conditions

The required fuel properties consist of a proximate analysis and an ultimate analysis expanded with the Hg and Cl contents, which we have. A complete time-

Table 3.3. Assigned flue gas composition for
Choctaw bituminous in the CRF.

Species	Mass %	Mole %
N ₂	71.6	76.5
CO ₂	20.8	14.1
H ₂ O	3.2	5.4
O ₂	4.2	3.9
CO, ppm	77	82
CH ₄ , ppm	0.6	1.0
C ₂ H ₂ , ppm	0.9	1.0
SO ₂ , ppm	1281	598
NO, ppm	252	251
HCl, ppm	7.6	6.2
Hg, ppb	5.3	0.8

temperature history for the flue gas from the furnace exit to the stack is required, and a measured thermal history for the CRF tests was presented in Fig. 3-2. The furnace rating, overall combustion efficiency, and economizer O₂ level or the flowrates of fuel and air are required to calculate the flue gas flowrate and composition. The composition of flue gas is evaluated from an equilibrium composition at the furnace exit temperature, then the major species are frozen throughout the simulation of Hg and Cl chemistry throughout the quench cycle. Complete emissions levels including HCl, CO, NO_x, and SO_x can also be specified in the input to the model if measurements are available; otherwise, the HCl and SO₂ levels are calculated from coal properties and default values are assigned for CO and NO. The flue gas composition assigned for the Choctaw bituminous in the CRF furnace appears in Table 3.3. The flowrates of fuel and air and the economizer O₂ level were used to evaluate the flue gas composition, except that the concentrations of CO, hydrocarbons, and NO were fixed at either measured or default values. (These species do not affect Hg/Cl chemistry under CRF test conditions.)

To initialize the kinetic calculations, the components in Table 3.3 were then processed through an equilibrium calculation at the user-specified furnace exhaust gas temperature (FEGT) to specify the initial values of the 96 atomic and molecular species included in the gas phase reaction mechanisms, including all Hg species. This composition determines the initial concentration for the simulation.

A bottom ash rejection rate and flyash LOI or UBC content are needed to calculate the loading of UBC in the flue gas. Unfortunately, neither quantity was

reported for the tests in the CRF. We estimated these values from our previous work with datasets from the CRF for Choctaw bituminous coal. The LOI used in our simulations is 4.2 wt. % and the bottom ash rejection is 5.6 wt. %. In addition, the sorbent type, surface area, quantity, and injection location is required. The surface area and particle size were not reported. We used values for these properties similar to those for activated carbons such as Darco FGD, which were a surface area of 600 m²/g and a particle diameter of 18 μm.

3.4.2 Adjustments to Operating Conditions

None of the CRF operating conditions were adjusted in the simulations of the CRF tests with MinPlus sorbent. The kinetic parameters specified from the bench-scale breakthrough tests were applied without tuning. But for baseline tests on inherent Hg control in this furnace, NEA's UBC mechanism did not accurately predict the baseline Hg speciation. The predicted Hg²⁺ level was only 5 % of the total Hg inventory at the FF inlet vs. a measured level of more than 50 %. Since we are focusing this extrapolation on MinPlus performance, such a large discrepancy in the baseline performance had to be eliminated. Although we already noted the omissions of several important test conditions, especially the LOI levels, we somewhat arbitrarily chose to modify the thermal history to increase the residence time to the FF from 5 to 6.8 s as seen in Fig. 3-6. The residence time was increased in the temperature range of 360 to 560 °C to increase the predicted extent of Hg oxidation on UBC without affecting the predictions for MinPlus at hotter temperatures.

In addition, the chlorine concentration in the flue gas was increased from the coal-based value of 6 ppmv to 23 ppmv to promote greater extents of Hg oxidation. Though this increase constitutes four times the HCl from the measured coal-Cl content, the range of chlorine levels from Choctaw coal under the similar conditions in previous CRF tests varied from 9 to 28 ppm, and the Cl increase in this work is well within that range.

3.4.3 Simulation Procedures

Reaction mechanisms are often discussed as symbolic diagrams of transformations among the chemical species in the system. What is discussed much less frequently is that these symbolic diagrams ultimately determine systems of coupled, nonlinear ordinary differential equations (ODEs) that are solved on computers with highly specialized numerical methods. To simulate Hg sorption on MinPlus, only two ODE's were solved simultaneously to describe Hg sorption on suspended sorbent particles. But NEA's

Figure 3-6. Modified CRF thermal history to rectify discrepancies in NEA's interpretation of the baseline CRF tests.

mechanism for Hg transformations on UBC particles includes both homogeneous and heterogeneous reactions, and 100 or so ODEs developed from the mechanism are solved to continuously describe the changes in the 100 or so species, including all Cl and Hg species, from the furnace exit to the stack. Virtually none of the conditions in these simulations are uniform in time, due mostly to the very large reduction in gas temperature along a gas cleaning system. In turn, these variations significantly affect the kinetics for Hg oxidation and sorption, which ultimately determine the Hg speciation along the gas cleaning system.

In the simulations for the CRF tests, the mechanism for Hg oxidation and sorption on UBC particles as described in Sec. 3.2.2 was implemented for the baseline tests, when no MinPlus was injected in the system. For the case with sorbent injection, two separate simulations were performed, one with the mechanism for Hg oxidation and sorption on UBC particles, and the other with the Hg sorption mechanism for MinPlus described in Sec. 3.2.1. The predicted Hg-P levels were evaluated as the sum of the contributions from both these calculation runs.

It is appropriate to sum the contributions to Hg-P from both mechanisms because,

Figure 3-7. Predicted Hg speciation along the CRF gas cleaning system based on NEA's mechanisms for Hg oxidation and sorption on suspended UBC.

as mentioned in Secs. 3.1.2 and 3.2.2, our Hg sorption mechanism for MinPlus does not differentiate between Hg^0 and Hg^{2+} , consistent with the observation that MinPlus injection did not affect the proportions of Hg^0 and Hg^{2+} vapors. Our mechanism for Hg transformations on UBC is not sensitive to the absolute Hg concentrations in the gas phase as long as the relative proportions of Hg^0 and Hg^{2+} vapors do not change. Therefore, Hg sorption on MinPlus does not depend on its chemistry on UBC particles and vice versa. It is also worth noting that no Hg-P forms on UBC in the relatively hot temperature window for MinPlus sorption.

3.4 Comparisons of Calculated and Measured Results

The predicted Hg speciation for the baseline test with the modified thermal history is shown in Fig. 3-7. At the furnace exit, all Hg is present as Hg^0 . During the initial 5 s when the temperature is above 300 °C, Hg^0 continuously oxidizes into Hg^{2+} , which reaches approximately 40 % of the total Hg inventory when the temperature reaches 300 °C. At that point, the mechanism shifts from Hg^{2+} production to the

Figure 3-8. Comparison of measured and calculated Hg speciation for baseline CRF tests for inherent Hg control.

desorption limit that only produces Hg-P. In Fig. 3-7, that transition is evident as a distinct change in the rate of Hg⁰ conversion beyond about 5s. For greater times, essentially all the Hg⁰ is converted into Hg-P. Note, however, that the time scale becomes fictitious across the FF because we are using an extended approach to equilibrium over 22 s to represent the near-instantaneous equilibration across the FF filtercake. So the predicted conversion across the FF should be read as the ultimate values for 29 s without regard for the pseudo-dynamic approach in time. For this case, adsorption equilibrium generates about 38 % Hg-P.

Baseline data are available only across the FF and are compared with the simulation results in Fig. 3-8. The 50 % extent of Hg⁰ oxidation at the FF inlet in the calculation results compares well to the measured value of 46 %. Only the calculated Hg-P level of 7 % is at odds with the absence of any measured Hg-P at the FF inlet. There is a corresponding deficit in the calculated Hg²⁺ level. At the FF outlet, the calculated total Hg vapor level is well within the measurement uncertainties of the measured emissions level, although the Hg⁰ is underpredicted by about 7% with a corresponding overestimate for Hg²⁺. All the discrepancies for the baseline test are within the measurement uncertainties, which are typically 10 -15 % of the total Hg inventory.

The predicted Hg speciation for tests with MinPlus injection based on the

Figure 3-9. Calculated Hg speciation for CRF tests with MinPlus injection at 22 lb/hr.

modified thermal history is shown in Fig. 3-9. These results reflect the 2-step reaction scheme for Hg sorption on MinPlus, but not the contributions from the mechanism for Hg oxidation and sorption on suspended UBC. The MinPlus injection rate was 22 lb/hr. Note that rate parameters specified from our interpretation of the packed-bed experiments were used in these simulations. Since there is no distinction between Hg^0 and Hg^{2+} in the MinPlus mechanism, a single Hg vapor lump appears in the figure. Elemental Hg is rapidly converted into Hg-P during the first 2s, when the flue gas is hotter than 400°C. Particulate-Hg quickly reaches 40 % and then remains uniform along the rest of the gas cleaning system. Even across the FF, there is no change in Hg speciation because the chemistry on UBC was omitted from this simulation case to highlight the behavior of MinPlus. In contrast to the exclusive production of Hg-P on UBC at lower temperatures, Hg-P is forms on MinPlus only at temperatures hotter than 400°C.

To estimate the actual performance of MinPlus in this test, the calculated Hg-P for inherent control was added to that from the MinPlus run in Fig. 3-9, with corresponding adjustments to the Hg vapor levels. Figure 3-10 shows the comparison of Hg-Vap and Hg-P data to the calculation results across the FF. With 22 lb/hr of MinPlus, about 45 %

Figure 3-10. Validation of predicted Hg speciation for CRF tests with 22 lb/hr MinPlus.

of the Hg inventory was present as Hg-P at the FF inlet, and 80 % of the Hg inventory was removed by the FF. The predicted Hg-P from Hg transformations on both UBC and MinPlus is 48 % at the FF inlet and 85 % at the stack, which are both in excellent agreement with the data.

3.5 Extrapolations

To the extent that the satisfactory comparison in Fig. 3-10 gives confidence to our representation of Hg transformations in the CRF, we next characterize variations in MinPlus injection rate and sorbent properties. All cases in this section were based on the operating conditions in Fig. 3-10. Predicted Hg removals for different MinPlus injection rates appear in Fig 3-11. For an injection rate of 8 lb/hr, only 20 % of the Hg is removed by the sorbent. Mercury removals increase in direct proportion to increases in MinPlus injection rate through 40 lb/hr. For greater injection rates, the predicted Hg removals start to saturate. The ultimate, asymptotic Hg removal is determined by the adsorption equilibrium for these particular operating conditions, although it is unclear whether or not the limit will be less than 100 % for larger injection rates than those in Fig. 3-11. In actuality, Hg removals for sorbent injection rarely exceed 92 – 95 %, which has been attributed to limitations in the particle dispersion in turbulent flows. Also, the predictions in Fig. 3-11 are for MinPlus only, without any contributions from Hg transformations on UBC. If typical Hg removals due to UBC were factored in, then all the Hg would have been predicted to be removed with 40 lb/hr of MinPlus.

Figure 3-11. Hg removals for various MinPlus injection rates for the operating conditions of Fig. 3-10.

Additional simulations were also performed to characterize the impact of MinPlus surface area. The reference value used in all previous calculations in this chapter for MinPlus is $600 \text{ m}^2/\text{g}$. Predicted Hg removals for internal areas from 100 to $1000 \text{ m}^2/\text{g}$ appear in Fig. 3-12. Qualitatively, increasing surface area is similar to increasing the sorbent injection rate. The Hg removal is only 10 % for $100 \text{ m}^2/\text{g}$, and increases for progressively greater surface areas. The approach to a saturation limit from the adsorption equilibrium is more gradual than it was for the greatest MinPlus injection rates. Since $1000 \text{ m}^2/\text{g}$ is close to the feasible upper limit on the surface areas of actual sorbent materials, MinPlus would not remove all the Hg for these operating conditions.

Figure 3-12. Sensitivity of predicted Hg removal to MinPlus surface areas under the operating conditions of Fig. 3-10.

4.0 SUMMARY AND FUTURE DEVELOPMENT

4.1 Summary

NEA's original role in this project was to use simulations to bridge the gap between performance tests of a sorbent called MinPlus at atmospheric pressure and the intended application of MinPlus for Hg control in warm gas cleaning systems on coal gasifiers. Once the lab tests at U. Utah established that the sorbent under evaluation, MinPlus, can only be used in the presence of O₂, a new, stronger imperative emerged. NEA therefore re-directed its efforts to identify a scheme that could introduce the required O₂ level into a stream of syngas, and maintain it throughout the time needed to remove Hg on MinPlus. This is a deeper challenge than the original assignment because syngas and O₂ do not normally co-exist at typical MinPlus operating conditions in gasifier applications: Due to several phase changes, MinPlus can only be used from 650 to 850°C; pressure is variable from 20 to 50 atm; and at least 0.5 s are needed for Hg removal.

NEA's proposed scheme uses a bank of fixed beds to continuously generate low levels of O₂ in syngas, followed by a second series of fixed beds of MinPlus to capture Hg. Fixed beds are used for the O₂ generation stage, because they provide the only means to uniformly disperse O₂ into the entire syngas stream while maintaining its concentration well below the explosion and flammability limits. It is imperative that the rich flammability limits are not exceeded even locally within the process stream to avoid significant adverse impacts on the quality of the syngas. The MinPlus is also applied in a fixed bed configuration because this approach offers extremely high surface area to volume ratios, which are needed to satisfy the constraint on the total Hg removal time.

NEA's proposed process for MinPlus applications to remove Hg from syngas streams appears to be feasible, pending further assessments of additional technical issues. The scheme utilizes BOC's CAR process to uniformly introduce sufficient O₂ to maintain MinPlus's Hg sorption activity under highly reducing conditions. This process directly releases O₂ from Perovskite packing which is regenerated via counterflow oxidation with O₂. By simultaneously operating manifolds of beds in the O₂ generation and regeneration modes, the O₂ level in syngas can be maintained continuously. This process is already under commercial development for oxyfuel furnaces to raise the O₂ level in recycled flue gas above the level in air. In fact, the required O₂ generation capacity for the application of MinPlus in gasifier cleaning systems is slightly smaller than that for the oxyfuel applications, and commercial designs are already available to satisfy this requirement.

Most important, we found that the O₂ lifetimes in syngas from Shell and GEPS gasifiers provided sufficient time for Hg sorption on MinPlus, based on a detailed reaction mechanism for syngas reforming. For Shell gasifier conditions, up to 0.5 s was available for Hg sorption for temperatures up to 700°C. And for the very high operating pressure of GEPS gasifiers, the O₂ levels reached a stable saturation limit that persisted for at least 2 s provided that the temperature was no hotter than 700°C. The limit was 170 ppm O₂ at 700°C but only 70 ppm at 600°C. The limit's existence was found to be governed by elevated pressure, and limits only appeared for the GEPS cleaning system. Changing the O₂ injection rate off the baseline value of 1 % of the syngas stream did not elevate these saturation limits. Adverse impacts of O₂ injection on syngas quality were minimal, because the O₂ injection rates were so small; whereas the CO mole fractions diminished slightly the H₂ mole fractions increased for most conditions.

We suspect that the saturation limits reflect a delicate balance determined by the size of the oxyhydroxyl radical pool, which is a sensitive function of both temperature and pressure. Whether they are real or simply artifacts of obscure parameter assignments in the syngas reforming mechanism is difficult to establish, especially since this mechanism was not directly validated for stoichiometries as rich as the ones in these calculations. Bear in mind that radical pools would almost certainly be affected by Perovskite and MinPlus surfaces via heterogeneous recombination reactions, and such chemistry was not included here. For the time being, we emphasize the potential existence of stable O₂ levels in syngas for as long as a few seconds at the highest gasifier pressures, noting that the operating conditions that form them are still subject to large uncertainties.

Due to limitations of schedule and budget, additional important technical issues could not be fully evaluated at this stage. The O₂ level needed to maintain Minplus's Hg sorption activity was found to be no greater than 0.4 % at atmospheric pressure under O₂/N₂ mixtures. To maintain the same O₂ partial pressure, this threshold could be reduced to 170 ppm at 23.5 atm and 100 ppm at 41 atm, which are the respective operating pressures of Shell and GEPS gasifiers. These O₂ levels could be maintained in syngas in the MinPlus temperature window, but this threshold still needs to be verified in additional testing.

BOC's CAR process to generate O₂ from Perovskite minerals is already developed for oxyfuel applications. However, a major uncertainty is whether or not syngas components will react heterogeneously with oxidized Perovskites under MinPlus operating conditions. It also remains to be demonstrated that Perovskites may be

regenerated with O₂ under hot gas cleaning conditions without steam washing.

Test data from U. Utah indicated that Hg sorption activities for MinPlus at 700°C were in the same range as the maximum activity at 900°C. In addition, both equilibrium Hg adsorption capacities and intrinsic sorption kinetics need to be monitored for temperatures from 600 to 750°C at elevated pressures to provide the rate data needed to design a fixed bed of MinPlus.

Since NEA did not have access to the kind of lab-scale kinetic data needed to pursue a preliminary design of a MinPlus bed for Hg control in gasifier streams, we demonstrated the extrapolations needed to scale-up Hg control with MinPlus from lab-scale to pilot-scale furnaces, rather than for gasifiers. Somewhat unexpectedly, there were problems in the simulation results for baseline tests, without MinPlus injection. These were rectified by adjusting the gas cleaning conditions. Ultimately, the MinPlus sorption kinetics specified by interpreting the lab-scale breakthrough tests were used without tuning to predict MinPlus performance across a FF in the pilot-scale tests.

2.1 Recommendations for Further Development

Several essential pieces of information are needed to advance NEA's MinPlus application scheme further, as follows:

- 1) The threshold O₂ level needed to sustain MinPlus's Hg sorption performance needs to be better quantified. Currently, it is known only to be no greater than 0.4 % O₂.
- 2) We also need to know if syngas components affect the Hg sorption activity of MinPlus, or if MinPlus otherwise sustains heterogeneous chemistry with syngas components.
- 3) Since the O₂ partial pressures needed to sustain MinPlus's Hg sorption activity are comparable to the O₂ saturation limits for GEPS gasifier conditions, the existence of these limits should be verified in tests. We also need to verify that elevated pressures are essential to their existence, as evident in our model calculations.
- 4) A major uncertainty is whether or not syngas components will react heterogeneously with oxidized Perovskites under MinPlus operating conditions. It also remains to be demonstrated that Perovskites may be regenerated with O₂ under hot gas cleaning conditions, particularly elevated pressures, without steam washing.

- 5) Both equilibrium Hg adsorption capacities and intrinsic sorption kinetics need to be monitored for temperatures from 600 to 750°C at elevated pressures to provide the rate data needed to design a fixed bed of MinPlus.
- 6) Once the basic kinetic data on MinPlus sorption at elevated pressures, it needs to be incorporated into more comprehensive simulations as a basis to extrapolate to a broad domain of warm gas cleaning conditions in gasification systems.

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APPENDIX B

Table 1. The results of equilibrium constants for Hg, HgCl and HgCl₂ adsorptions on 4×4×2 CaO cluster model within 250 K ~ 600 K (ln(K_{eq}), ΔS and ΔG vs. 1000/T)

1000/T	ln(K _{eq})			ΔS(cal/molK)			ΔG(kcal/molK)		
	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂
4.000	20.543	76.514	30.316	-10.316	12.627	5.690	-10.205	-38.008	-15.059
3.636	19.292	68.899	27.230	-10.602	12.788	5.828	-10.541	-37.648	-14.879
3.354	18.331	62.983	24.831	-10.846	12.922	5.942	-10.860	-37.313	-14.710
3.333	18.261	62.549	24.655	-10.865	12.932	5.950	-10.885	-37.286	-14.697
3.077	17.399	57.172	22.473	-11.108	13.062	6.060	-11.236	-36.920	-14.512
2.857	16.670	52.559	20.599	-11.335	13.180	6.161	-11.593	-36.552	-14.325
2.667	16.045	48.557	18.972	-11.546	13.290	6.255	-11.956	-36.181	-14.136
2.500	15.505	45.053	17.545	-11.744	13.392	6.342	-12.323	-35.808	-13.945
2.353	15.034	41.958	16.284	-11.930	13.488	6.424	-12.696	-35.433	-13.752
2.222	14.621	39.205	15.161	-12.106	13.578	6.502	-13.074	-35.055	-13.556
2.105	14.256	36.739	14.153	-12.273	13.664	6.576	-13.455	-34.675	-13.358
2.000	13.932	34.517	13.245	-12.431	13.745	6.647	-13.841	-34.293	-13.158
1.905	13.642	32.505	12.420	-12.581	13.823	6.715	-14.231	-33.908	-12.957
1.818	13.382	30.674	11.669	-12.724	13.897	6.780	-14.624	-33.522	-12.753
1.739	13.147	29.000	10.982	-12.861	13.968	6.843	-15.021	-33.133	-12.547
1.667	12.935	27.464	10.351	-12.992	14.037	6.903	-15.421	-32.743	-12.340

Table 2. The results of equilibrium constants for Hg, HgCl and HgCl₂ adsorptions on 5×5×2 CaO cluster model within 250 K ~ 600 K (ln(K_{eq}), ΔS and ΔG vs. 1000/T)

1000/T	ln(K _{eq})			ΔS(cal/molK)			ΔG(kcal/molK)		
	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂
4.000	15.506	72.851	35.268	-5.566	4.498	5.384	-7.702	-36.189	-17.519
3.636	14.389	66.030	31.662	-5.642	4.482	5.688	-7.863	-36.080	-17.301
3.354	13.526	60.736	28.852	-5.709	4.466	5.945	-8.013	-35.982	-17.093
3.333	13.463	60.349	28.646	-5.714	4.464	5.965	-8.025	-35.974	-17.076
3.077	12.682	55.543	26.084	-5.781	4.445	6.219	-8.190	-35.869	-16.844
2.857	12.016	51.426	23.879	-5.845	4.425	6.454	-8.357	-35.764	-16.606
2.667	11.442	47.859	21.959	-5.905	4.405	6.674	-8.526	-35.661	-16.362
2.500	10.941	44.739	20.273	-5.962	4.385	6.881	-8.696	-35.559	-16.113
2.353	10.501	41.987	18.779	-6.016	4.367	7.076	-8.868	-35.457	-15.858
2.222	10.112	39.541	17.444	-6.068	4.349	7.261	-9.042	-35.356	-15.598
2.105	9.765	37.354	16.246	-6.117	4.332	7.437	-9.217	-35.255	-15.333
2.000	9.454	35.385	15.162	-6.164	4.316	7.604	-9.393	-35.155	-15.063
1.905	9.175	33.604	14.177	-6.209	4.301	7.764	-9.571	-35.055	-14.789
1.818	8.921	31.986	13.278	-6.252	4.287	7.918	-9.750	-34.955	-14.511
1.739	8.691	30.508	12.453	-6.293	4.273	8.065	-9.930	-34.856	-14.228
1.667	8.481	29.154	11.694	-6.333	4.260	8.207	-10.111	-34.757	-13.941

Table 3. The results of equilibrium constants for Hg, HgCl and HgCl₂ adsorptions on 5×5×2 periodic slab within 250 K ~ 600 K (ln(K_{eq}), ΔS and ΔG vs. 1000/T)

1000/T	ln(K _{eq})			ΔS(cal/molK)			ΔG(kcal/molK)		
	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂	Hg	HgCl	HgCl ₂
4.000	18.132	63.501	22.688	-10.064	0.451	4.114	-9.007	-31.544	-11.270
3.636	17.074	57.728	20.299	-10.323	0.393	4.387	-9.330	-31.544	-11.092
3.354	16.263	53.245	18.436	-10.544	0.339	4.618	-9.635	-31.544	-10.922
3.333	16.204	52.917	18.299	-10.562	0.335	4.636	-9.659	-31.544	-10.908
3.077	15.478	48.846	16.597	-10.783	0.280	4.864	-9.995	-31.544	-10.718
2.857	14.864	45.356	15.130	-10.989	0.227	5.075	-10.337	-31.543	-10.522
2.667	14.339	42.332	13.852	-11.183	0.178	5.273	-10.684	-31.543	-10.321
2.500	13.886	39.686	12.726	-11.365	0.131	5.459	-11.037	-31.542	-10.115
2.353	13.492	37.351	11.728	-11.536	0.088	5.635	-11.394	-31.542	-9.904
2.222	13.147	35.275	10.834	-11.699	0.048	5.803	-11.755	-31.541	-9.687
2.105	12.842	33.418	10.030	-11.853	0.010	5.962	-12.121	-31.541	-9.467
2.000	12.572	31.746	9.302	-12.000	-0.026	6.114	-12.491	-31.540	-9.241
1.905	12.332	30.234	8.639	-12.139	-0.059	6.261	-12.864	-31.539	-9.012
1.818	12.116	28.859	8.032	-12.273	-0.090	6.401	-13.241	-31.539	-8.778
1.739	11.922	27.604	7.475	-12.401	-0.119	6.536	-13.622	-31.538	-8.540
1.667	11.747	26.453	6.961	-12.524	-0.147	6.667	-14.005	-31.538	-8.298

Table 4. Changed atomic charges based on Mulliken and Hirshfeld population analysis of Hg, HgCl and HgCl₂ adsorption models on fixed 5×5 CaO periodic slabs obtained with LDA/PWC functionals

	Mulliken			Hirshfeld		
	CaO-Hg	CaO-HgCl	CaO-HgCl ₂	CaO-Hg	CaO-HgCl	CaO-HgCl ₂
Ca 1	0.00	0.01	0.01	0.00	0.01	0.01
Ca 2	0.00	0.02	0.02	0.00	0.01	0.01
Ca 3	0.00	0.01	0.01	0.00	0.01	0.00
Ca 4	0.02	0.03	0.02	0.01	0.01	0.01
Ca 5	0.01	0.03	0.03	0.00	0.02	0.00
Ca 6	0.01	0.03	0.03	0.00	0.00	0.01
Ca 7	-0.02	-0.01	-0.01	-0.04	-0.03	-0.02
Ca 8	-0.02	0.01	-0.01	-0.04	-0.02	-0.02
Ca 9	0.01	0.02	0.01	0.00	0.01	0.01
Ca 10	-0.02	-0.01	0.00	-0.04	-0.03	-0.12
Ca 11	0.01	0.02	0.01	0.00	0.02	0.01
Ca 12	-0.02	0.02	0.00	-0.04	-0.12	-0.12
Ca 13	0.00	0.01	0.01	0.00	0.01	0.01
Ca 14	0.00	0.01	0.01	0.00	0.01	0.01
Ca 15	0.00	0.01	0.01	0.00	0.01	0.01
Ca 16	0.00	0.02	0.01	0.00	0.01	0.01
O 17	0.01	0.01	0.02	0.00	0.01	0.01
O 18	0.01	0.01	0.02	0.00	0.01	0.01
O 19	0.01	0.01	0.02	0.00	0.01	0.01
O 20	0.01	0.06	0.02	0.00	0.03	0.01
O 21	0.00	0.00	0.00	0.00	0.01	0.00
O 22	0.00	0.00	0.00	0.00	0.01	0.00
O 23	0.00	0.01	0.00	0.00	0.01	0.00
O 24	0.00	0.00	0.00	0.00	0.01	0.00
O 25	0.00	0.01	0.01	0.00	0.01	0.01
O 26	0.00	0.01	0.01	0.00	0.01	0.01
O 27	0.00	0.00	0.01	0.00	0.01	0.00
O 28	0.00	0.01	0.01	0.00	0.01	0.00
O 29	0.00	0.00	0.00	0.00	0.01	0.01
O 30	0.00	0.03	0.04	0.00	0.02	0.03
O 31	0.00	0.00	0.01	0.00	0.01	0.01
O 32	0.05	0.06	0.04	0.03	0.04	0.02
Hg	-0.07	-0.29	-0.18	0.09	-0.16	-0.10
Cl 1		-0.17	-0.08		0.02	0.08
Cl 2			-0.08			0.08

Table 5. Changed atomic charges based on Mulliken and Hirshfeld population analysis of Hg, HgCl and HgCl₂ adsorption models on relaxed 5×5 CaO periodic slabs obtained with LDA/PWC functionals

	Mulliken			Hirshfeld		
	CaO-Hg	CaO-HgCl	CaO-HgCl ₂	CaO-Hg	CaO-HgCl	CaO-HgCl ₂
Ca 1	-0.01	0.01	0.01	-0.05	0.01	0.01
Ca 2	-0.01	0.03	0.04	-0.05	0.01	0.01
Ca 3	0.01	0.01	0.01	0.01	0.01	0.01
Ca 4	0.01	0.03	0.03	0.01	0.03	0.04
Ca 5	0.01	0.02	0.02	0.00	0.02	0.02
Ca 6	0.02	0.02	0.02	0.01	0.02	0.02
Ca 7	0.01	0.00	-0.01	0.00	-0.04	-0.03
Ca 8	0.01	0.00	-0.01	0.00	-0.04	-0.03
Ca 9	0.01	0.01	0.01	0.00	0.01	0.01
Ca 10	0.01	-0.02	0.01	0.00	-0.07	-0.10
Ca 11	0.01	0.02	0.01	0.00	0.02	0.01
Ca 12	0.01	0.01	0.01	0.00	-0.10	-0.10
Ca 13	0.01	0.01	0.01	0.01	0.01	0.00
Ca 14	-0.01	0.01	0.01	-0.05	0.01	0.00
Ca 15	0.01	0.02	0.01	0.01	0.00	0.00
Ca 16	-0.01	0.02	0.01	-0.05	0.00	0.00
O 17	0.00	0.02	0.01	0.00	0.01	0.00
O 18	0.00	0.02	0.01	0.00	0.01	0.00
O 19	0.00	0.00	0.01	0.00	0.01	0.00
O 20	0.00	0.00	0.01	0.00	0.01	0.00
O 21	0.01	0.00	0.00	0.00	0.00	0.00
O 22	0.01	0.00	0.00	0.00	0.00	0.00
O 23	0.01	0.01	0.00	0.00	0.00	0.00
O 24	0.01	0.01	0.00	0.00	0.00	0.00
O 25	-0.01	0.01	0.00	0.00	0.01	0.00
O 26	0.11	0.01	0.00	0.06	0.01	0.00
O 27	0.00	0.00	-0.01	0.00	0.00	0.00
O 28	-0.01	0.00	-0.01	0.00	0.00	0.00
O 29	0.00	-0.01	-0.01	0.00	0.00	0.00
O 30	0.00	-0.03	-0.05	0.00	0.01	0.00
O 31	0.00	-0.02	-0.02	0.00	0.00	0.00
O 32	0.00	0.16	0.16	0.00	0.10	0.11
Hg	-0.15	-0.26	-0.11	0.06	-0.10	-0.07
Cl 1		-0.13	-0.11		0.03	0.03
Cl 2			-0.11			0.03

Figure 1. Initial and final 3D-pictures of CaO(44)-Hg, CaO(55)-HgCl and CaO(periodic)-HgCl₂ models with LDA/PWC functional

Initial and final pictures of CaO(44)-Hg

Initial and final pictures of CaO(55)-HgCl

Initial and final pictures of CaO(periodic)-HgCl₂

Figure 2. The top views and side views of optimized geometries of (a) Hg, (b) HgCl and (c) HgCl₂ adsorptions on relaxed periodic slab