

SORBENTS FOR MERCURY REMOVAL FROM FLUE GAS

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TABLE OF CONTENTS

ABSTRACT.....	1
1.0 INTRODUCTION	2
2.0 COMMERCIAL SORBENTS.....	7
3.0 SORBENT RESEARCH & DEVELOPMENT	8
3.1 Experimental.....	9
3.1.1 Contacting System	9
3.1.2 Mercury Spiking System	9
3.1.3 Analytical Technique	10
3.1.4 Characterization of Spent Sorbent	11
3.2 Physical and Chemical Properties of Mercury	11
3.3 Promoters.....	15
3.3.1 Halides.....	15

3.3.1.1 Iodine/Iodine Pentoxide	19
3.3.2 Sulfur/Sulfides	21
3.3.3 Lime/Barium Oxide	21
3.4 Sorbents.....	22
3.4.1 Carbon Based Sorbents.....	22
3.4.2 Noble Metals.....	23
3.4.3 Base Metals.....	25
3.4.4 Metalloids.....	26
3.4.5 Oxides.....	26
3.4.5.1 Manganese Dioxide and Hopcalite	27
3.4.5.2 Vanadium Oxides	29
3.4.5.3 Chemically Promoted	31
3.4.5.4 Silica.....	31
3.4.5.5 Fly Ashes.....	32
4.0 ECONOMIC CONSIDERATIONS	32
5.0 RECOMMENDATIONS FOR FUTURE SORBENT RESEARCH	35

5.1 Near-Term Sorbent Candidates.....	35
5.1.1 Partially Reducible Base Metal Oxides.....	36
5.1.2 Fly Ashes.....	36
5.1.3 Halides.....	37
5.1.4 Activated Carbons.....	37
5.2 Long-Term Potential Sorbents.....	37
5.2.1 Non-Reducible Oxides.....	37
5.2.2 Non-Reducible Oxides Promoted With Halides	39
5.2.3 Noble Metal Monoliths	41
5.3 Long-Term Sequestration	41
5.4 Contacting Method	41
DISCLAIMER.....	42
ACKNOWLEDGEMENTS	42
REFERENCES.....	42

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ABSTRACT

A review of the various promoters and sorbents examined for the removal of mercury from flue gas is presented. Commercial sorbent processes are described along with the chemistry of the various sorbent-mercury interactions. Novel sorbents for removing mercury from flue gas are suggested. Since activated carbons are expensive, alternate sorbents and/or improved activated carbons are needed. Because of their lower cost, sorbent development work can focus on base metal oxides and halides. Additionally, the long-term sequestration of the mercury on the sorbent needs to be addressed. Contacting methods between the flue gas and the sorbent also merit investigation.

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1.0 INTRODUCTION

Mercury is present in coal, in municipal solid waste, and in medical wastes. Mercury emissions occur when coal, municipal solid waste, or medical wastes are burned. Mercury emissions also occur as a result of certain manufacturing processes, such as copper, zinc, and lead smelting, and the electrochemical production of chlorine and sodium hydroxide from brine using mercury electrodes. Natural phenomena such as volcanic eruptions, geysers, and wild fires also contribute to the mercury found in the environment.

Mercury is a powerful neurotoxin. Precipitation removes mercury from the atmosphere, and deposits it into lakes, where it can enter the food chain in the form of methylmercury and accumulate in fish. The form of mercury in the flue gas, be it elemental mercury or an oxidized form such as mercuric chloride, has a large effect on its dispersal and ultimate fate. Excessive exposure to mercury can cause tremors, loss of coordination, blurred vision, personality changes, and in severe cases, death [1]. The threshold exposure limit for elemental mercury is 0.1 mg/m^3 air. Oxidized forms of mercury (such as mercuric chloride and organometallic compounds) are generally more toxic than elemental mercury. There is a lack of data on the effects of chronic low level exposure to mercury [1,2]. Many uses for mercury and its compounds, such as in pigments, biocides for paints, in seed disinfectants, and in batteries, have been restricted or banned [1].

The concentration of mercury in U.S. coals varies widely, but is quite low, typically ranging from 0.02 to 1.0 ppm, with a mean value of 0.13 ppm [3]. A typical eastern-bituminous mid-sulfur coal contains 0.1 ppm Hg [80]. Earlier analytical work showed that most coals supplied to power plants contain an average of 0.2 ppm mercury [4,5]. Coals from the western U.S. can be very low in mercury, many containing less than 0.05 ppm Hg [3,4,5]. However, because of the large volume of coal which is burned, it is estimated that 51 tons of mercury per year are emitted into the atmosphere by U.S. electric utilities. This represents approximately 21% of the annual anthropogenic U.S. mercury emissions, the remainder coming from municipal waste combustion (23%), medical waste incinerators (27%), industrial boilers (12%), and manufacturing activities (13%) [6].

The concentrations of mercury in flue gas emanating from the combustion of municipal solid waste and especially medical waste are often far higher than in flue gas originating from coal. However, the restrictions on certain uses for mercury as in batteries and paints, are slowly lowering the emissions of mercury from municipal waste combustion. EPA has just

established a federal mercury standard for municipal waste combustors of 50 micrograms/Nm³. The development of alternatives to mercury-containing thermometers, sphygmomanometers, dental amalgams, and antiseptics, should gradually reduce the emissions of mercury from medical waste incinerators. In addition, EPA has recently mandated stringent reduction of mercury emissions from medical waste incinerators [70]. The 2,400 existing medical waste incinerators will have five years to comply with the new regulation; new incinerators will have six months to comply. On the other hand, the usage of coal by electric utilities is projected to increase over the next 15 years. In addition, the most recent data shows that coal-fired utilities are now the largest anthropogenic source of mercury emissions in the United States. These facts, coupled with studies performed under Title III of the 1990 Clean Air Act Amendments, may impact the regulation of mercury emissions in flue gas produced from coal combustion.

The total concentration of mercury in the flue gas from coal-fired power plants is on the order of 1 ppb. The primary forms of mercury in flue gas are elemental mercury and mercuric chloride. Flue gas is an oxidizing environment, as excess oxygen is typically used in the combustion of coal, municipal solid waste, and medical waste. The oxidizing nature of flue gas precludes the use of base metal sorbents for mercury abatement. The composition of an untreated flue gas is shown in Table 1 [7,66].

Table 1 Typical Flue Gas Composition From a Coal-Fired Utility

H ₂ O	5 - 6 %
O ₂	3 - 4 %
CO ₂	15 - 16 %
Total Hg	1 ppb
CO	25 ppm
Hydrocarbons	10 ppm
HCl	100 ppm
SO ₂	1000 ppm
SO ₃	20 ppm
NO _x	500 ppm
N ₂	balance

The temperature of flue gas in a typical coal utility system will vary widely along the process path. The flue gas will exit the

furnace at approximately 2500°F. Heat is then extracted from the flue gas. Flue gas will leave the economizer at around 800°F. Flue gas exits the air preheater at about 450°F. Unscrubbed flue gas enters the stack at around 300°F in order to be above the acid dew point. Therefore, a sorbent that removes mercury from flue gas could operate anywhere between 300 to 2500°F, depending upon where the sorbent contacts the flue gas.

The available control technologies for the removal of mercury from flue gas are fabric filters, scrubbing solutions, electric discharges, and dry sorbents. Only dry sorbents and scrubbing solutions have demonstrated consistently high levels of mercury removal. This report reviews the current state of dry sorbent technology.

Commercial sorbents for the removal of mercury from flue gas from waste incinerators are based on activated carbon. High surface area activated carbons are expensive, and can be effectively regenerated only a few times. Activated carbons are general adsorbents. Various activated carbons and chars will adsorb mercury from flue gas. Activated carbons will also adsorb other species in flue gas, such as SO₂, water, oxygen, arsenic and other volatile trace metals, and radon. The concentration of mercury in the flue gas emanating from a waste incinerator is on the order of 100 ppb; the sorbent utilization is usually low, and the costs associated with an activated carbon process are high. The process economics (expressed as dollars per pound of mercury removed) for an activated carbon process for the removal of mercury from a more dilute stream (1 ppb Hg flue gas from a utility) will be even worse.

Many sorbents can remove mercury from flue gas. A sorbent can capture mercury from flue gas via amalgamation (alloying), absorption, physical adsorption, chemical adsorption, or by chemical reaction. Several of these processes can occur simultaneously. For example, mercury may be first absorbed, and then physisorbed before being chemisorbed. Therefore, it can be useful to identify the predominant or rate determining step for each sorbent. The characteristic temperature, enthalpy, activation energy, and number of adsorbate layers are distinguishing features of these processes. Mercury is present in flue gas as both elemental mercury and oxidized mercury. It is not a trivial matter to identify the main process by which a sorbent removes mercury because many reaction and transport processes can be occurring simultaneously, involving both elemental and oxidized mercury.

Physisorption is analogous to condensation, and is a low temperature process. At atmospheric pressure, physisorption will occur at a significant rate only at temperatures well below 675°F, the boiling point of mercury at 1 atmosphere. More than

one layer of adsorbate can be physisorbed on a surface. The heat of physisorption, as well as its activation energy are small. Amalgamation is analogous to the dissolution of a gas in a liquid, and is also a low-temperature process. Absorption is the diffusion and transient capture of mercury vapors in the complex pore maze network of a sorbent. Chemisorption can be envisioned as a surface reaction, limited to a monolayer. Chemisorption and chemical reaction can occur over a wide range of temperatures. Chemisorption and chemical reaction typically have higher activation energies and heats of reaction than does physisorption.

For example, noble metal wires such as gold will amalgamate (alloy) with elemental mercury at room temperature, whereas thin gold films will adsorb mercury as a monolayer. Certain sorbents remove mercury by forming a chemical compound. For example, selenium will remove mercury from flue gases by the formation of mercury selenide (HgSe) at 1200°F . Sulfur, on the other hand, will react with mercury at room temperature. Some sorbents can work by a combination of mechanisms. Porous, high surface-area aluminosilicates may absorb and physisorb mercury at lower (300°F) temperatures, and possibly react with mercury to form mercury aluminosilicates at higher ($1300\text{--}2200^{\circ}\text{F}$) temperatures. It should be noted that coal ash, containing both unburned carbon and aluminosilicate compounds, could be a potential mercury sorbent.

Other compounds act as promoters for the removal of mercury from flue gas. Lime is used in conjunction with activated carbon in some commercial sorbent processes [8,9,10]. For example, lime has been demonstrated to reduce mercury emissions in coal flue gas, even though lime neither sorbs nor reacts directly with mercury. It is speculated that lime aids in the removal of mercury by reacting with acid gases such as SO_2 that compete for adsorption with mercury on both coal ash, unburned carbon particles, and activated carbon sorbents. Another example of promoters are the halides and sulfides, which are often dispersed on high surface-area carbons and aluminosilicates.

Sorbent capacities are usually low. The capacities reported in the literature are typically on the order of 100 micrograms Hg/gram sorbent, and range from 10^{-6} to 10^{-2} gram Hg/gram sorbent [15,16,22,24,29,33,38]. A 3000:1 activated carbon/mercury ratio has been suggested as necessary to attain efficient mercury removal from the flue gas arising during the combustion of coal [14]. Other researchers report that a 50,000:1 activated carbon/mercury ratio is necessary to achieve a high level of mercury removal from the flue gas arising during the combustion of coal [87].

The removal of mercury from flue gas can be depicted by the equation:



where product represents either amalgam, absorbed mercury, physisorbed mercury, chemisorbed mercury, or a chemical reaction product.

The sorbent/mercury ratio is inordinately high (or equivalently the experimentally determined sorbent capacities are inordinately low) because:

- 1) The concentration of mercury in the flue gas is so low, on the order of 1 ppb. Therefore, a large sorbent/mercury molar ratio is needed to drive the reaction to the right (Le Chatelier's Principle).
- 2) The residence time for contact between the flue gas and sorbent is very short, on the order of 10 seconds for spray driers, and 1 second for sorbent injection into a flue gas duct (kinetics). The large surface area possessed within the pores of activated carbon sorbents may be inaccessible due to the short residence times.
- 3) Sorbent utilization or selectivity is usually low because of competing adsorbate species in the flue gas; i.e., acid gases adsorb on activated carbons, oxygen adsorbs on metals, and water will be sorbed by aluminosilicates.
- 4) Sorbents deactivate over time due to factors such as pore plugging, sintering, and poisoning, resulting in a loss of active surface area.
- 5) For chemical adsorption, all isotherms predict low sorbent capacities at low partial pressures of adsorbate. Rate of adsorption is a monotonic function of adsorbate partial pressure, increasing with increasing partial pressure. Therefore, capacity, determined by the difference between the rates of adsorption and desorption over time, will exhibit a similar pattern.

The extreme dilution (ppb Hg) and short residence time reduce effective contact, or number of collisions, between mercury and the sorbent. This implies the need for low sorbent cost, improved sorbent utilization, and better means of gas-sorbent contact.

In order for a sorbent to attain wide usage for mercury removal from flue gas, it must be highly active, selective, and cost effective. It may be advantageous for the sorbent to be regenerable. If the sorbent is disposable, its final form should be safe (non-toxic) and stable. An ideal sorbent would possess a long life (slow deactivation/high capacity). A sorbent possessing all of these characteristics has not been identified thus far. This topical report will discuss the status of sorbent

research and development and suggest new areas for research.

2.0 COMMERCIAL SORBENTS

The commercial use of sorbents for mercury removal from flue gas produced from coal burning is in its infancy. Most of the commercial uses of these sorbents are for the removal of mercury arising from the combustion of municipal or medical waste.

Sorbalit is a sorbent comprised of hydrated lime and a sulfur-promoted activated carbon [8]. This sorbent was developed by Marker Umwelttechnik of Germany. The sorbent is used to remove acid gases, mercury, and/or dioxins. The sorbent operates at temperatures from 275 - 465°F, and can be introduced into flue gas via duct injection or spray drying [8]. Hydrated lime is far cheaper than the high surface area sulfur-promoted activated carbon, and normally comprises most of the sorbent. The surface area of the hydrated lime is on the order of 1 m²/gram, whereas the surface area of the promoted activated carbon is approximately 1000 m²/gram. The surface area of a typical sorbalit sorbent containing 4 wt.% activated carbon is 35 m²/gram [8].

Hydrated lime removes acid gases, such as sulfur dioxide and HCl, via the following chemical reactions:



The activated carbon removes flue gas mercury and organic pollutants such as dioxins via adsorption. The activated carbon is porous and possesses a high surface area. The surface has active sites for the adsorption of organic toxins such as dioxins, and sites for the adsorption of heavy metals such as mercury. Activated carbons also will adsorb acid gases. These acid gases compete with mercury for adsorption on carbon. The hydrated lime in sorbalit greatly increases the effectiveness of the carbon for mercury adsorption by removing the acid gases. (More information on the role of lime in the removal of mercury is presented in Section 3.3.3.). A sulfur promoter is added to the activated carbon. This enhances the ability of the activated carbon to remove elemental mercury via the reaction:



This ability is important because elemental mercury in the flue gas is more difficult to capture than mercuric chloride, the predominant mercury species in flue gas originating from municipal waste incinerators [8].

A similar process for the removal of mercury from flue gas is the RC/Teller system, developed by Research Cottrell Companies in New Jersey. Lime, activated carbon, and Tesisorb are used in combination to control acid gas, mercury, and dioxin emissions from medical waste incinerators [9]. Tesisorb is a baghouse filter cake modifying agent [10].

The GE-Mitsui-BF activated coke process can remove SO_x , NO_x , mercury, HCl, furans, and dioxins from flue gas [11,12,13]. The surface area of the activated coke is on the order of 150-250 m^2/gram , which is about one fourth that of a typical high surface area activated carbon [11]. The activated coke is also one third the price of a typical high surface area activated carbon [11,12]. Several pilot tests have shown that the Mitsui activated coke can remove mercury and NO_x from flue gas emanating from waste incinerators [11]. At temperatures between 302 -356°F, mercury removal efficiencies of 80-99+% were observed [11,12].

The GE-Mitsui-BF process can be configured to: 1) remove both SO_x and NO_x using two activated coke beds, 2) remove NO_x using a single activated coke bed, or, 3) remove SO_x using a single activated coke bed. It is claimed that any of these configurations can also remove mercury and dioxins with high efficiency [11].

The ultimate disposal of mercury recovered from the flue gas is an important issue. In the GE-Mitsui-BF process, spent activated coke is regenerated by heating to 750°F [12]. The off-gas from the sorbent regenerator will have a high concentration of mercury. GE proposes treatment of this gas with a commercially available selenium filter [12]. Mercury is removed by the filter with 98% efficiency [12], and forms the product mercuric selenide. Mercuric selenide is a stable compound, and the spent filter can be sent to an approved disposal facility.

3.0 SORBENT RESEARCH AND DEVELOPMENT

A wide array of materials have been examined as potential sorbents for the removal of gas phase mercury. These materials include activated carbons [14-24], noble metals [22,25-33], base metals [30,34,35], selenium [36], and metal oxides [37-42].

In addition, many chemicals that increase the capacity of activated carbons for mercury have been examined. These chemicals, which include halides [24,25,40,43,44], sulfides [23,28], sulfur [16-18,21-22,40-42,64,73], and lime [8,9,16], are called promoters. The experimental apparatus and scale of the different investigations varied considerably.

3.1 Experimental

The scale of the various investigations ranges from bench top to plant scale. The scale of the investigation often dictates the choice of contacting system, spiking system, and analytical technique. The characterization of the used sorbent can also yield valuable information on the mechanism of sorbent-mercury interactions.

3.1.1 Contacting System

A means of contacting the gas with the sorbent is necessary to investigate the removal of mercury. For lab-scale investigations, a packed bed reactor is commonly used. In pilot plant scale work, duct injection or spray drying is often used to contact the sorbent with the gas. The choice of a contacting system, essentially a reactor design issue, is a critical factor in determining mercury removal by the sorbent. This is because the choice of the contacting system and its location within the combustion facility will determine sorbent temperature, mercury speciation, and flue gas-sorbent contact time.

3.1.2 Mercury Spiking System

A method for obtaining a steady concentration of mercury in the simulated flue gas is a prerequisite for investigation of sorbents. The two most common devices for obtaining a steady concentration of elemental mercury are saturators and permeation tubes. In a saturator, elemental mercury comes into equilibrium with a carrier gas, and the partial pressure of mercury in the saturated carrier gas will equal the vapor pressure of mercury. Mercury diffuses through the teflon walls of a permeation tube. Diffusion vials are often used when a steady concentration of mercuric chloride is desired. Mercuric chloride effuses through a small orifice in a diffusion vial. Other studies have examined the fate of mercury during the combustion of coal, municipal solid waste, and medical waste at plant scale. In these cases mercury volatilizes during the combustion of the feed, and a spiking system is necessary only if a higher, controlled level of mercury is desired.

3.1.3 Analytical Technique

A detection system for elemental and oxidized mercury is necessary in order to determine the removal by the sorbent. The most common technique used for the determination of elemental mercury is ultraviolet spectrophotometry. Ultra violet methods include atomic absorption spectrophotometry (AAS) and atomic fluorescence spectrophotometry (AFS). These techniques rely upon the absorption of 253.7nm ultraviolet radiation by elemental mercury. This absorption wavelength is specific for elemental mercury.

There are broad band absorbers such as SO₂ and aromatic hydrocarbons, which will also absorb 253.7nm UV radiation, thereby potentially interfering with the determination of mercury. Other substances present in flue gas and capable of attenuating UV light at a wavelength of 253.7nm are smoke, soot, fine particulates, water vapor, and nitrogen dioxide [27]. One method to alleviate the interference caused by SO₂ is the gold amalgamation technique. First, mercury is selectively collected on gold. Next, mercury is volatilized from gold to the UV detector. The Zeeman effect can also be employed to correct for other species absorbing or scattering 253.7 nm ultraviolet light [27].

Another approach employed for the determination of elemental mercury is the resistivity method. The Jerome analyzer uses this approach. A thin gold film, in the presence of mercury vapor, will undergo an increase in electrical resistance proportional to the mass of mercury in the sample [45].

The determination of oxidized forms of mercury is more complex. The commonly available analytical techniques, atomic absorption, and atomic fluorescence spectrophotometry, detect elemental mercury. Therefore, an indirect method is used to determine oxidized mercury. First, elemental mercury is determined by either AAS or AFS. Next, total mercury (elemental plus oxidized) is determined by reducing any oxidized mercury to elemental mercury. A comparison of these measurements allows the determination of oxidized mercury by difference.

A mass spectrometer could also be used as an on-line, continuous detector for both elemental mercury and mercuric chloride in flue gas. However, the 1ppb concentration of mercury in flue gas is near the detection limit of many mass spectrometers [27, 84]. An ion trap mass spectrometer could offer a detection limit of around 1 ppt of mercury [82], making this type of mass spectrometer a potential continuous analyzer for both elemental and oxidized mercury in flue gas.

3.1.4 Characterization of Spent Sorbent

Physical and chemical analysis of the used sorbent can provide information on the nature of mercury-sorbent interactions. The continuous on-line measurement of mercury, as it is thermally desorbed from a spent sorbent, will provide useful information on the presence of mercury surface species. The determination of mercury volatilized from the sorbent can be done by an on-line atomic fluorescence spectrophotometer [47] or by a mass spectrometer [27]. The temperature at which mercury volatilizes from the spent sorbent can suggest the presence of an amalgam, absorbed mercury, physisorbed mercury, chemisorbed mercury, or a specific mercury compound.

X-ray absorption fine structure spectroscopy (XAFS) has also been applied to obtain information on surface species present on used sorbents [69]. The absorption of x-rays is related to elemental mercury concentration via Beer's law. Interpretation of the spectra can provide information on mercury species. X-ray diffraction can be used to detect changes in the bulk composition of the sorbent.

Also, most of the techniques used to characterize catalysts can be applied to analyze sorbents, and these include BET surface area measurement and porosity determination. The physical characterization of fresh sorbent can provide a baseline for comparison with spent sorbent, and can suggest mechanisms such as sintering and pore plugging that cause sorbent deactivation.

3.2 Physical and Chemical Properties of Mercury

A brief review of the physical and chemical properties of mercury and its common compounds is shown in Tables 2 and 3. Table 4 shows some multiple oxides and double halides of mercury. These properties and compounds help explain many sorbent-mercury interactions.

Table 2 Properties of Mercury

Normal melting point-	36°F
Normal boiling point	675°F

Critical Temperature, T_c	3051°F
Critical Pressure, P_c	732 atm
Pauling Electronegativity	2.1
Common Oxidation States	0 elemental mercury Hg^0 +1 mercurous form Hg_2^{2+} +2 mercuric form Hg^{2+}
Standard Reduction Potential	+0.851 volts, which is more noble than most metals
Monoatomic vapor, like the noble gases	
Solubility in water	20 µg/liter at 68°F; 64 µg/liter at 77°F; 600 µg/l at 212°F
Vapor pressure at 75°F	2.2×10^{-6} atm
Bond length at -51°F	3.005 Å
Common forms:	Hg, HgS, HgSe, HgTe, HgCl_2 , HgCl, HgBr_2 , HgBr, HgI ₂ , Hgl, HgO, K_2HgI_4 , and $(\text{CH}_3)_2\text{Hg}$
Amalgams	with noble metals and most base metals

Table 3 Properties of Oxidized Mercury

HgS

melting point	1082°F
solubility in water	0.000001 gram/100 cc @ 64°F
$\Delta G_f =$	-8.8 kcal/mol at 77°F
$\Delta H_f =$	-10.7 kcal/mol at 77°F

HgCl₂

melting point	529°F
boiling point	576°F
solubility in water	6.9 gram/100 cc @ 68°F
$\Delta G_f =$	-42.2 kcal/mol at 77°F
$\Delta H_f =$	-53.4 kcal/mol at 77°F



melting point	457°F
boiling point	612°F
solubility in water	0.61 gram/100 cc @ 77°F
$\Delta G_f = -38.8$	kcal/mol at 77°F
$\Delta H_f = -40.68$	kcal/mol at 77°F



melting point	498°F
boiling point	669°F
$\Delta G_f = -24$	kcal/mol at 77°F
$\Delta H_f = -25.3$	kcal/mol at 77°F



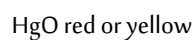
sublimation temperature	752°F
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sublimation temperature	653°F
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sublimation temperature	104°F
decomposition temperature	554°F
$\Delta G_f = -26.53$	kcal/mol at 77°F
$\Delta H_f = -28.88$	kcal/mol at 77°F



decomposition temperature	932°F
solubility in water	0.0053 gram/100 cc @ 77°F
$\Delta G_{f \text{ red}} = -13.94$	kcal/mol at 77°F
$\Delta H_{f \text{ red}} = -21.6$	kcal/mol at 77°F

Table 4a Some Multiple Oxides of Mercury

<u>Oxide</u>	<u>Formula</u>	<u>Reference</u>
Mercurous orthohexatantalate	4Hg ₂ O 3Ta ₂ O ₅ 5H ₂ O	[46]

Mercuric orthohexatantalate	$4\text{HgO} \cdot 3\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	[46]
Mercuric diarsenite	$\text{Hg}_5\text{As}_2\text{O}_8$	[46]
Mercurous orthoarsenite	Hg_3AsO_3	[46]
Mercury (II) hydrogen arsenate	HgHAsO_4	[61]
Mercuric tritungstate	$2\text{HgO} \cdot 3\text{WO}_3$	[46]
Mercuric molybdate	HgMoO_4	[46]
Mercurous molybdate	Hg_2MoO_4	[46]
Mercuric chromate	HgCrO_4	[46,61]
Mercury (II) dichromate	HgCr_2O_7	[61]
Mercury octopermanganite	$\text{HgO} \cdot 8\text{MnO}_2 \cdot 3\text{H}_2\text{O}$	[46]
Mercuric henapermanganite	$\text{HgO} \cdot 11\text{MnO}_2 \cdot 6\text{H}_2\text{O}$	[46]
Mercury niobium oxide	$\text{Hg}_2\text{Nb}_2\text{O}_7$	[72]
Mercury tantalum oxide	$\text{Hg}_2\text{Ta}_2\text{O}_7$	[72]
Mercury antimony oxide	$\text{Hg}_2\text{Sb}_2\text{O}_7$	[72]
Mercurous ferrate	Hg_2FeO_4	[46]
Mercuric ferrate	HgFeO_4	[46]
Mercurous stannate	$\text{Hg}_2\text{SnO}_3 \cdot 5\text{H}_2\text{O}$	[46]
Mercuric stannate	$\text{HgSnO}_3 \cdot 6\text{H}_2\text{O}$	[46]
Mercurous borododecatungstate	$\text{Hg}_9[\text{B}(\text{W}_2\text{O}_7)_6] \cdot 12.5\text{H}_2\text{O}$	[46]
Mercury (II) iodate	$\text{Hg}(\text{IO}_3)_2$	[61]
Barium mercurate	BaHgO_2	[62]
Calcium mercurate	CaHgO_2	[62]
Mercury barium copper oxide	$\text{HgBa}_2\text{CuO}_4$	[61]
Mercury barium calcium copper oxides	$\text{HgBa}_2\text{CaCu}_2\text{O}_6$	[61]
	$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	[61]
	$\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10}$	[61]
Mercury vanadates	HgVO_3	[55]
	HgV_2O_6	[54,55]
	Hg_2VO_4	[55]
	$\text{Hg}_2\text{V}_2\text{O}_7$	[54]

	$\text{Hg}_4\text{V}_2\text{O}_9$	[54]
	$\text{Hg}_6\text{V}_2\text{O}_{11}$	[54]
Mercury silicate (speculated)	HgSiO_3	[80,81]

Table 4b Some Halides of Mercury

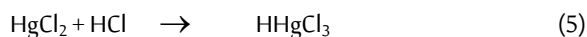
<u>Halide</u>	<u>Formula</u>	<u>Reference</u>
Mercuric cobaltous tetraiodide	$\text{HgI}_2 \text{ CoI}_2 \cdot 6\text{H}_2\text{O}$	[46]
Mercuric ferric bromide	$\text{HgBr}_2 \text{ FeBr}_2 \cdot 4\text{H}_2\text{O}$	[46]
Mercuric nickel hexaiodide	$2\text{HgI}_2 \text{ NiI}_2 \cdot 6\text{H}_2\text{O}$	[46]
Mercuric nickel tetraiodide	$\text{HgI}_2 \text{ NiI}_2 \cdot 6\text{H}_2\text{O}$	[46]
Mercuric thalious iodide	$\text{HgI}_2 \text{ TlI}$	[46]
Mercuric tetrachloroplumbite	$\text{HgCl}_2 \text{ PbCl}_2$	[46]
Silver iodomercurate	Ag_2HgI_4	[49,61]
Cuprous iodomercurate	$\text{Cu}_2(\text{HgI}_4)$	[60]
Potassium triiodomercurate	KHgI_3	[46]
Potassium iodomercurate (II)	$\text{K}_2(\text{HgI}_4) \cdot 2\text{H}_2\text{O}$	[60,61]
Sodium chloromercurates	NaHgCl_3	[46]
	Na_2HgCl_4	[46]
Hydrotrichloromercuric acid	HHgCl_3	[46]

3.3 Promoters

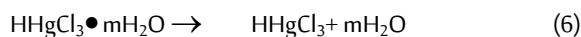
Many chemicals have been examined for their ability to increase the capacity of activated carbon. These materials include halides, halogens, sulfur, sulfides, and lime. The distinction between sorbent and promoter is somewhat arbitrary, as both contribute to the capture of mercury. A promoter can be defined as a chemical dispersed on or within a high surface area substrate, which aids in the removal of mercury from flue gas. These substrates can include high surface area activated carbons and aluminosilicates. Promoters increase the chemisorption and chemical reaction of mercury on the sorbents.

3.3.1 Halides

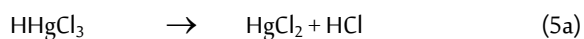
Mercuric chloride is soluble in water, and is even more soluble in hydrochloric acid. The increased solubility in hydrochloric acid is due to the reaction between mercuric chloride and hydrochloric acid, which forms the complex hydrotrichloromercuric acid [46]:



Hydrotrichloromercuric acid can precipitate from solution to form needle-like crystals [46]. The compound, usually associated with water, will dehydrate around 212°F,

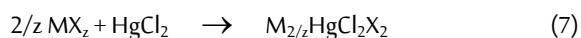


and decompose at somewhat higher temperatures,



Braman showed that HCl treated Chromosorb-W, a diatomite chromatographic packing, will adsorb mercuric chloride vapors at 70°F [25]. Quimby demonstrated that HCl treated activated carbon will adsorb mercuric chloride from air at 300°F [24].

Many metal halides react in a similar manner with mercuric chloride [46]. Some of the metal halides have been tested for their ability to promote activated carbon or aluminosilicate sorbents, or as sorbents by themselves. These compounds include alkali metal salts [24,25,40,43], alkaline earth salts [40], copper halides [24,43], iron halides [24], aluminum halides [24], and noble metal halides [44]. It is likely that base metal halides aid in the removal of mercuric chloride by chemical reaction to form a metal halomercurate:



For univalent metals such as sodium, the reaction can also proceed as for HCl:



where: M is the metal

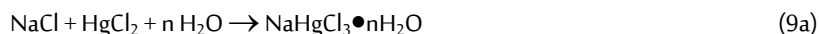
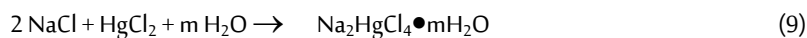
X is the halogen of the metal halide

z is the metal valence, +1 or +2

For example, sodium chloride is known to react with mercuric chloride to form sodium chloromercurates, e.g.,



The product, sodium chloromercurate, is typically hydrated so that the reactions can also be written as:



Some of the many halides of mercury are shown in Table 4. The thermal stability of the halomercurates above 212°F is questionable. At temperatures of 212 to 400°F, it is probable that metal halides chemisorb mercuric chloride. Other common halomercurates are cuprous iodomercurate, $\text{Cu}_2(\text{HgI}_4)$, potassium iodomercurate, $\text{K}_2(\text{HgI}_4) \bullet 2\text{H}_2\text{O}$, and silver iodomercurate, Ag_2HgI_4 . Cuprous iodomercurate formerly found application in thermosensitive paints, as it changes color reversibly from bright red to brown at 160°F, suggesting a decomposition temperature well above 160°F [60]. Potassium iodomercurate was once a widely used antiseptic [60]. Silver iodomercurate is a silver cation conducting solid electrolyte at 480°F, implying a decomposition temperature above 480°F [49].

It is likely that alkali and alkaline earth halides chemisorb elemental mercury. Elemental mercury is known to amalgamate with most base metals [46,53]. Mercury will react with the alkali metals, albeit under reducing conditions, to form the compounds Li_2Hg , Na_2Hg , K_2Hg , Rb_2Hg , and Cs_2Hg [53]. Mercury will react with the halogens to form mercuric or mercurous halides [46,53]. The surface of a base metal halide will contain unbalanced forces due to the abrupt change in structure from the bulk, as well as roughness on a microscopic scale. These forces can be balanced by the adsorption of mercury. The base metal halides are, therefore, potential sorbents for elemental mercury. Livengood demonstrated that pumice promoted with either calcium chloride or potassium iodide will effectively remove elemental mercury from argon at 158°F [40].

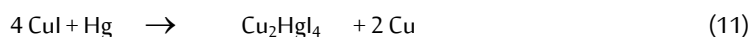
Unpromoted pumice removed little mercury [40].

It can be speculated that other base metal halides, such as copper iodide, react with elemental mercury. Crisp [43] used CuI impregnated paper to detect and determine elemental mercury in air at room temperature. The paper was found to change color in the presence of elemental mercury in concentrations of 50 - 100 micrograms/m³; a pink stain was produced. The reflectance of the stain was correlated with the amount of mercury in the air. The authors state that the nature of the chemical reaction between mercury and copper iodide is not known with certainty.

There are a limited number of possible reactants and products which could account for a pink stain; these are copper iodide, mercuric iodide and cuprous iodomercurate. Mercuric iodide is a brilliant red powder, and could form from the reaction:

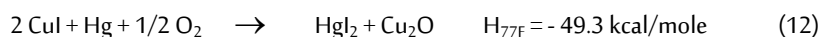


Copper [I] iodide has a white color. The combination of mercuric iodide (red) product and unreacted copper iodide (white) could result in a pink stain. Another possibility is the reaction:

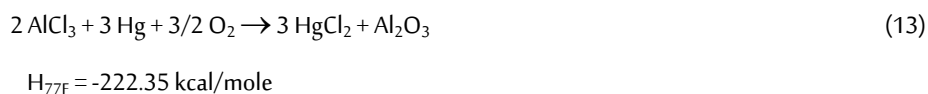


Cuprous iodomercurate is a bright red or orange powder [60]. The combination of cuprous iodomercurate (red) product and unreacted copper iodide (white) could also result in a pink stain.

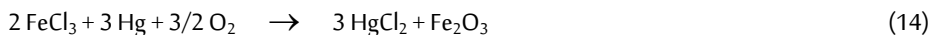
Under harsher flue gas conditions, the base metal halide sorbent could form metal oxide, further enhancing the thermodynamics of mercury sequestration. For example, reaction (10) could be rewritten as



For aluminum chloride sorbent, the reaction could be presented as:

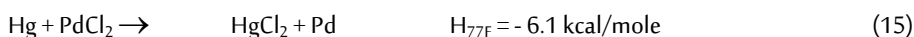


For iron chloride sorbent, the reaction could be presented as:



$$\Delta H_{77^\circ\text{F}} = -164.6 \text{ kcal/mole}$$

In the case of noble metal halides, chemical reaction accounts for the removal of mercury. For palladium chloride, the reaction can be written as:



A palladium chloride filter has been used to remove elemental mercury from air at room temperature [44]. Mercuric chloride is a volatile solid with melting point of 529°F, so that the sorbent must be used at low temperatures such as 77°F. The reaction is stated to be irreversible [44].

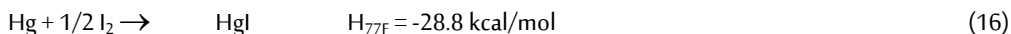
3.3.1.1 Iodine/Iodine Pentoxide

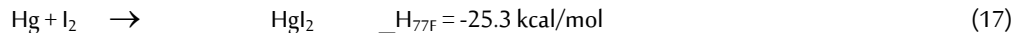
Mercury will readily react with the halogens to form mercuric and mercurous halides. The normal melting points and boiling points of the halogens are shown in Table 5. The temperature of flue gas in a coal-fired utility plant can range from 2500°F exiting the combustion chamber down to 300°F at the stack. Most of the halogens are too volatile to be used as promoters in their elemental state. Only iodine possesses a sufficiently high boiling point to enable its use as a promoter in an activated carbon flue gas sorbent.

Table 5 Melting Points/Boiling Points of the Halogens

F ₂	melting point -369°F	boiling point -305°F
Cl ₂	melting point -151°F	boiling point -30°F
Br ₂	melting point 19°F	boiling point 138°F
I ₂	melting point 236°F	boiling point 364°F

An iodine promoter would increase the sorbent capacity for elemental mercury by the chemical reactions:





Another advantage of iodine promoters is the lower volatility of mercuric iodide (boiling point 670°F) versus other mercuric halides. This enhances the stability of the spent sorbent having iodine as a promoter.

One of the only stable halogen oxides is iodine pentoxide, I_2O_5 , $\Delta H_f = -42.5 \text{ kcal/mol}$ at 77°F, a white crystalline solid with a decomposition temperature of 572°F [53]. This is sufficiently high to permit its use as a promoter. At the decomposition temperature, iodine pentoxide melts to form iodine and oxygen [53]. It is speculated that iodine pentoxide aids in the capture of elemental mercury via the chemical reaction:



Elemental iodine promoters may form iodine pentoxide under oxidizing flue gas conditions.

In addition, mercury iodates are known to exist. For example, mercury (II) iodate, $\text{Hg}_2(\text{IO}_3)_2$, is a yellow solid, and will decompose at 482°F. The formation of mercury iodate could represent another pathway for mercury capture by iodine pentoxide.

Activated carbons have been promoted with both iodine and potassium iodide [48]. This combination of promoters may permit removal of mercury at higher operating temperatures. An activated carbon promoted with both iodine and potassium iodide was recently used to remove elemental mercury from argon at 290°F [47]. In this case the following reactions can occur:



The decomposition temperatures of potassium iodomercurate (II) and potassium triiodomercurate are around 212°F. The

decomposition temperature of mercurous iodide is 554°F. Desorption of mercury from a spent activated carbon sorbent, promoted with both iodine and potassium iodide, has been observed at 212°F and 547°F [47]. This suggests that reactions 19, 19a, 16, 20 and 20a are occurring during the capture of mercury by the sorbent.

3.3.2 Sulfur/Sulfides

Sulfur and sulfides are often added to activated carbons to increase the capacity for elemental mercury. Sulfur aids in the capture of elemental mercury by chemical reaction to form mercuric sulfide [16-18,21-22,40-42,64,73]:



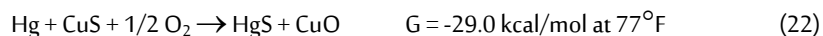
Mercuric sulfide is a solid with a melting point of 1082°F.

Elemental sulfur has several allotropes, including S₈, S₆, and S₂. It has been suggested that the terminal sulfur atoms are the active sites for reaction with elemental mercury. Therefore, the shorter allotrope promoters S₂ and S₆, having a greater percentage of terminal sulfur atoms, are hypothesized as being more reactive than the longer allotrope promoter S₈ [64].

Sulfides such as copper sulfide also aid in the removal of elemental mercury by chemical reaction [23,28]:



Reaction (21) is said to be reversible [23]. This is borne out by the thermodynamics of reaction (21); $\Delta G = +2.89 \text{ kcal/mol}$ at 77°F. This suggests that CuS could aid in the removal of mercury in an oxidizing flue gas environment by the reaction:



Mercury is said to "flour" or "sicken" when contacted with the sulfides of arsenic, copper, zinc, lead, and bismuth [46]. This suggests reaction with these sulfides to form mercuric sulfide.

3.3.3 Lime/Barium Oxide

Activated carbons are general adsorbents, and will sorb acid gases as well as heavy metals including mercury. The removal of acid gases by lime proceeds via chemical reaction:



The acid gases sulfur dioxide and hydrogen chloride may compete with mercury for adsorption on carbon. Therefore, the removal of acid gases by lime could enhance the capture of mercury by carbon.

Calcium chloride, the product of hydrogen chloride neutralization by lime, is a known promoter for the capture of mercury. Calcium chloride will likely chemisorb elemental mercury. Calcium chloride will likely increase the removal of mercuric chloride by the chemical reaction:



or by chemisorption.

Barium oxide has been found to react with elemental mercury at 1472°F to form barium mercurate, BaHgO₂ [62]. Sealed ampules containing a stoichiometric mixture of barium oxide and mercuric oxide were heated to 1472°F for one hour. Barium mercurate is completely hydrolyzed within several hours in air at 77°F [62]. The x-ray diffraction pattern shows that barium mercurate is isostructural to calcium mercurate, CaHgO₂ [62].

It is unlikely that the mechanism behind lime's ability to promote mercury removal is chemical reaction to form calcium mercurate. Flue gas contains water, and any calcium mercurate formed would likely hydrolyze as does barium mercurate.

3.4 Sorbents

Many materials have been examined as potential sorbents for the removal of mercury from flue gas. These materials include many activated carbons, noble metals, base metals, metalloids, and oxides.

3.4.1 Carbon Based Sorbents

Activated carbons have been the most thoroughly studied sorbent for the capture of mercury. Many activated carbons and

chars have been examined for their ability to remove mercury from flue gas. The carbon can originate from the coal [11-13,16,52,71,79], plant materials such as coconut shell, pine wood, or grains [16,48,79], and polymers [21] such as saran. The method of activation is often a high temperature steam treatment [11-13,48,52,79]. The manufacture of activated carbons is a complex art. Parameters critical to the production of activated carbons include particle size, carbon source, carbonization conditions, activation treatment, and binder additions. The activated carbons usually possess high surface areas on the order of $1000 \text{ m}^2/\text{gram}$.

The temperatures at which these sorbents are reported to be active range from 70 to 500°F [8-24,47,52,64,73]. An upper temperature limit on the use of activated carbons exists because:

- 1) The potential for ignition at higher temperatures,
- 2) Destruction of the internal pore network and loss of surface area at elevated temperatures,
- 3) Volatilization of sorbed mercury at elevated temperatures, and
- 4) Volatilization of chemical promoter at elevated temperatures.

The capacity of activated carbons has been reported to range from 1 to 17,000 micrograms Hg/gram [15,16,24,47,64,73]. The regenerability of activated carbons are generally limited to a few cycles [23]. Activated coke is similar to activated carbon. Activated coke has a lower surface area and a lower cost than activated carbon, and is used in the GE-Mitsui process for flue gas clean-up [52].

A sorbent can also be produced from the unburned carbon contained in fly ash [71]. The properties of this carbon obtained as a combustion by-product are currently under investigation.

3.4.2 Noble Metals

The noble metals are gold, silver, platinum, rhodium, and palladium. These metals have been employed as mercury sorbents at temperatures between 68 and 275°F . Noble metal wires remove elemental mercury by forming an alloy (amalgam). Noble metal films adsorb mercury as a monolayer.

Gold sorbs both elemental and oxidized forms of mercury, but not to the same extent. Gold is often employed to collect mercury for its determination in analytical systems. Mercury is then thermally desorbed, often at $800 - 900^\circ\text{F}$.

Gold is a poor adsorber of oxygen [49], an inactive hydrocarbon oxidation catalyst [49], and a good adsorber of oxidized forms of mercury [25,30,33]. Other noble metals, such as platinum, palladium, and silver, are good adsorbers of oxygen [49], are active hydrocarbon catalysts [49], and are poorer adsorbers of oxidized mercury [25,30,33]. This suggests that surface oxygen acts as a poison for the adsorption of oxidized mercury on metals.

The sorption of mercury on gold has been examined at room temperature by Chao [22], Braman [25], Williston [26], Henriques [29,30], Yan [32], and Dumarey [33]. Roberts studied the sorption of mercury on a gold coated monolith at 275°F [31,68].

The capacity of thin noble metal films for mercury has been reported as 1 - 10 micrograms Hg/gram [29,33]. The capacity of the noble metals for elemental mercury is somewhat higher than for oxidized forms such as mercuric chloride [29]. Noble metal sorbents exhibit excellent regenerability [26,31,32,33,68]. Mercury is often collected on gold, thermally desorbed, and sent to a UV detector for its analytical determination.

Roberts recently reported the capacity of a gold monolith for mercury as 0.1 gram Hg/gram [68]. The most concentrated mercury-gold alloy is 0.16 gram Hg/gram [60]. This suggests that the monolith removes mercury by forming an amalgam.

It has been suggested that the hardness of the noble metal is a good indicator for its tendency to amalgamate with mercury [82]. Gold is the softest of the noble metals, and possesses the greatest tendency to form amalgams. These results are shown in Table 6.

Table 6 Hardness and the Tendency to Form Amalgams

Noble Metal	Typical Hardness, HV [85]	Tendency to Amalgamate [83]
Au	25	Highest
Ag	27	
Pt	48	
Pd	50	
Rh	130	Lowest

3.4.3 Base Metals

Most base metals can alloy (amalgamate) with elemental mercury. Unfortunately, a surface oxide layer greatly diminishes the activity of base metals to form amalgams. Chips of Cu, Zn, Cd, Sn, Pb, and Bi were investigated for their ability to remove trace quantities of elemental mercury from air at 68°F [30]. Copper initially removed 100% of elemental mercury in air, but quickly deactivated as the metal became covered with a layer of copper oxide [30]. Zinc, cadmium, tin, lead, and bismuth removed little mercury [30]. The authors speculate that because the chips were heated in air during their preparation, a stubborn oxide layer inhibited the amalgamation with mercury in air at 68°F [30]. This means that gas phase oxygen can greatly reduce the activity of these sorbents for amalgamation. Copper, zinc, cadmium, tin, lead, and bismuth all removed little methyl mercury and methyl mercuric chloride from air [30]. Base metals are not practical flue gas sorbents because flue gas produced by coal combustion is an oxidizing environment. That a surface oxide layer on Cu, Zn, Cd, Bi, Pb, and Sn inhibits amalgamation at 68°F in no way excludes the possibility that many base metal oxides will adsorb or react with mercury. Table 4 lists some multiple oxides of mercury.

The alkali metals form amalgams with elemental mercury in definite proportions, Li_2Hg , Na_2Hg , K_2Hg , Rb_2Hg , and Cs_2Hg , suggesting chemical reaction under reducing conditions.

The only base metals having little tendency to amalgamate with mercury are iron, niobium, vanadium, molybdenum, tantalum, and tungsten, which compose most of the group VB and VIB elements. The inertness of iron is utilized in the commercial packaging of mercury in iron containers [53].

The base metals iron, niobium, vanadium, molybdenum, tantalum, and tungsten all possess high melting points, and exhibit little tendency to amalgamate with mercury. Melting point temperature is a good indicator of the tendency to form amalgams. Metals which are soft and have a low melting temperature have the greatest tendency to form amalgams.

Table 7 Melting Point and the Tendency of Base Metals to Form Amalgams

Metal	Melting Point °F	Forms Amalgam [53]
Sn	450	Yes
Bi	520	Yes

Cd	610	Yes
Pb	622	Yes
Zn	786	Yes
Al	1220	Yes
Cu	1981	Yes
Fe	2795	No
V	3110	No
Nb	4474	No
Mo	4748	No
Ta	5162	No
W	6098	No

3.4.4 Metalloids

The mechanism for mercury removal by a selenium sorbent is chemical reaction:



Selenium has been examined for the reduction of mercury emissions from a Swedish crematoria [36]. The source of mercury emissions are dental amalgams. Mercury emissions were reduced from the order of 30 to 5 mg/m³ by placing a Se ampoule in the coffins. The reaction occurs primarily in the gas phase at 1200°F.

Hogland claims that the spent sorbent, mercury selenide, has no adverse environmental effects [36]. Other reports state that mercury selenide is toxic [65].

Selenium is also the proposed sorbent for the removal of mercury during the regeneration of spent activated coke in the GE-Mitsui-BF activated coke process [12]. Selenium filters have been successfully used for the reduction of mercury emissions from lead smelters in Sweden [6].

3.4.5 Oxides

Several oxides have been studied for their ability to capture gas phase mercury species. These oxides are manganese dioxide [37], hopcalite [38], vanadium oxides [39], alumina and chemically promoted inert oxides [25,40-42], and silica [80,81]. Barium titanate has been found to remove mercury from wastewater at 86 - 140°F, possibly by ion exchange [63].

3.4.5.1 Manganese Dioxide and Hopcalite

Manganese dioxide has been reported to sorb mercury and its compounds from both air and argon at 68°F [37,38]. Hopcalite, which is a mixture of oxides containing 3 parts MnO₂, 2 parts CuO, and small amounts of CoO and Ag₂O, has also been reported to remove both elemental and oxidized mercury from air at 68°F [38].

Janssen [37] used manganese dioxide as a sorbent for mercury determination in air. A packed bed reactor, consisting of a tube filled with 2 grams of MnO₂, was used to sample air at 68°F in an alkali chloride electrolysis plant. The concentration of mercury in the electrolysis plant was about 50 micrograms Hg/m³. AAS was used to detect mercury. The determination of total mercury in air via MnO₂ sorbent was nearly identical to the determination by an activated carbon sorbent.

Further experiments were performed by spiking argon gas with various mercury compounds. It was found that the MnO₂ sorbent removed nearly 100% of elemental mercury, mercuric chloride, methyl mercuric chloride, phenylmercuric chloride, and methylmercuric benzoate from argon at 68°F. Permeation tubes were used to spike the argon gas.

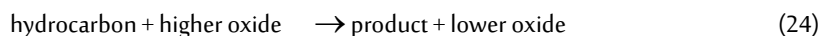
Rathje [38] examined hopcalite as a sorbent to collect elemental mercury from air. A packed bed reactor in the form of a small glass tube filled with hopcalite granules was utilized to collect elemental mercury from air at 68°F. Air is drawn through the tube by a small pump. The tube can be attached to a worker's safety glasses for monitoring of personal mercury exposure. Atomic absorption spectrometry was used to measure the mercury collected by the hopcalite sorbent. Concentrated nitric acid was used to remove the mercury collected by the sorbent.

Elemental mercury was introduced into the reactor by dilution of a saturated air-mercury vapor mixture; i.e., an elemental mercury bath saturator. The concentrations of elemental mercury in air ranged from 0.04 to 2.6 mg/m³. The sorbent was able to remove nearly all of the elemental mercury introduced into the packed bed containing 0.5 gram of hopcalite. This

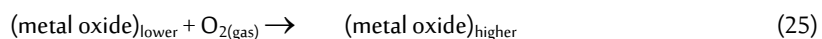
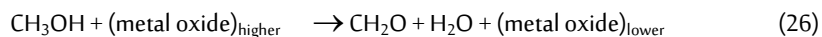
quantity of sorbent quantitatively removed up to 100 micrograms of mercury, corresponding to a capacity of 200 micrograms Hg/gram of sorbent.

Manganese dioxide is an oxidizing agent. Manganese has several common oxide forms, such as MnO_2 , Mn_2O_3 , Mn_3O_4 , and MnO . Manganese dioxide is a widely used catalyst for the selective oxidation of allylic and benzylic alcohols to aldehydes or ketones [53].

Lattice oxygen has been demonstrated to be a versatile and mild oxidant in the partial oxidation of hydrocarbons. The Mars-Maessen mechanism is commonly proposed to explain the action of partial oxidation catalysts, and is shown below:



For example, the partial oxidation of methanol to formaldehyde over oxide catalysts proceeds via a Mars-Maessen mechanism:



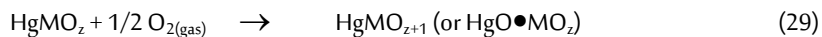
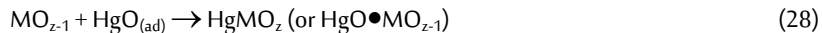
The first step of the mechanism is reduction of oxide by the hydrocarbon, forming the partial oxidation product and lower oxide. The second step is the reoxidation of the catalyst by gas phase oxygen. Note that the mechanism requires partial reduction of the oxide.

It can be speculated that in an analogous manner, there are multivalent partial oxidation catalyst oxides which behave in a similar way as mercury sorbents. It is proposed that these oxide sorbents capture mercury by:

- 1) First oxidizing elemental mercury with lattice oxygen
- 2) Then forming a binary or ternary oxide with mercuric oxide
- 3) Finally being reoxidized by gas phase oxygen

This mechanism can be written as:





where M is a multivalent metal possessing partial oxidation oxides such as manganese, vanadium, molybdenum, and bismuth.

First notice that this mechanism suggests that mercury can be captured in the absence of gas phase oxygen, steps 27 and 28. Janssen [37] found that manganese dioxide will sorb both elemental and oxidized forms of mercury in the absence of gas phase oxygen, i.e., in argon. Similarly, partial oxidation catalyst oxides will also function in the absence of gas phase oxygen. Granite fed 2.2 % methanol in helium over the partial oxidation catalyst oxides bismuth oxide, yttria-bismuth oxide, and yttria-stabilized zirconia at 545°F, and was able to form formaldehyde for a period of hours [49].

Next notice that the spent sorbent, a double oxide of mercury, will be stable. The free energy of formation of the spent sorbent will be approximately:

$$\Delta G_{f \text{ spent sorbent}} = \Delta G_{f \text{ HgO}} + \Delta G_{f \text{ sorbent}} \quad (30)$$

The free energy of formation of the double oxide is negative and large, the sum of two negative terms. Rathje [38] used concentrated nitric acid to remove mercury from the spent hopcalite sorbent. Some of the multiple oxides of mercury are shown in Table 4. Note the existence of binary oxides of mercury with manganese, tin, iron, chromium, molybdenum, tungsten, arsenic, tantalum, and vanadium. Vanadium pentoxide is the other classic partial oxidation catalyst, and is discussed next.

3.4.5.2 Vanadium Oxides

Vanadium oxides have not been extensively studied as sorbents for the removal of mercury from flue gas [39]. Most of the available information states that mercuric oxide will react with vanadium oxides to form the binary oxide mercury vanadates [39,54,55,56,72]. Angenault [54] reports that $\text{Hg}_2\text{V}_2\text{O}_7$ is formed by heating the mixture $2 \text{HgO}/\text{V}_2\text{O}_5$ for 7 minutes at 750°F. Heating the mixture $4 \text{HgO}/\text{V}_2\text{O}_5$ for 15 minutes at 750°F results in the formation of $\text{Hg}_4\text{V}_2\text{O}_9$. Thermal gravimetric analysis in air indicates that the onset of thermal decomposition occurs earlier for the high Hg/V mercury vanadates, viz [54]:

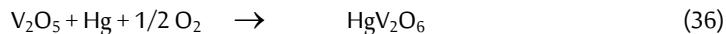
Hg/V = 1/2	HgV ₂ O ₆ :	860°F
Hg/V = 2	Hg ₄ V ₂ O ₉ :	625°F
Hg/V = 3	Hg ₆ V ₂ O ₁₁ :	480°F

The mercury to vanadium ratio indicates the thermal stability of the mercury vanadate.

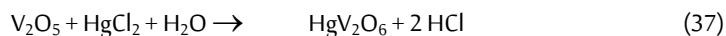
There are many mercury vanadate compounds reported in the literature [54,55,56] such as HgVO₃, Hg₂VO₄, Hg₂V₂O₇, Hg₄V₂O₉, and Hg₆V₂O₁₁. The composition of these compounds suggests that one mole of vanadium dioxide or vanadium pentoxide reacts with one or more moles of mercuric oxide as follows:



Wessels [55] formed the mercury vanadates HgVO₃ and Hg₂VO₄ by heating mercuric oxide with an amorphous mercury vanadate of the approximate composition HgV₂O₆ at 750°F for one week. A corona discharge was recently used to oxidize elemental mercury to mercuric oxide [39]. The mercuric oxide then reacted with vanadium pentoxide supported on alumina. Zinc and cadmium vanadates ZnV₂O₆ and CdV₂O₆ are also known to exist [54,55]. This suggests the possibility that vanadium pentoxide could also react with other heavy metals in addition to mercury. The cadmium vanadates are more difficult to form compared to the mercury vanadates. CdV₂O₆ is formed by heating CdO with V₂O₅ in air at 1200°F for 24 hours [54]. There is scant information on the sorption of elemental mercury or mercuric chloride by vanadium oxides. In addition, there is little information on the sorption of mercury by vanadium oxides in flue gas. It can be speculated that vanadium pentoxide will react with elemental mercury and oxygen to form mercury vanadate:



It is proposed that flue gas mercuric chloride and water could react with vanadium pentoxide viz:



3.4.5.3 Chemically Promoted

Insulator metal oxides such as alumina, aluminosilicates, silica, and lime show little activity for mercury removal by themselves. However, when a promoter such as a halide, sulfide, or sulfur is dispersed on these materials, an active mercury sorbent is formed. The activity of relatively inexpensive high surface area materials such as alumina, silica, pumice, etc. to capture mercury is greatly enhanced by the use of halogen or sulfur promoters. This scheme enables the sorbents to be used at moderate temperatures of 70 - 200°F [25,40,41,42]. Livengood [40] examined several chemically impregnated pumices for their ability to remove elemental Hg from N₂ at 158°F. Permeation tubes were used to introduce elemental mercury into nitrogen. Pumice is vitrified ash; a porous volcanic glass, and exhibited a low capacity for elemental mercury. Pumice impregnated with either sulfur, potassium iodide, or calcium chloride exhibited a much larger capacity for elemental mercury. The concentration of mercury in N₂ sent to the packed bed was 33 micrograms/m³, as determined by a Jerome analyzer. The performances of the pumices were, in decreasing order of mercury removal after 30 minutes: 1% sulfur (100% removal), 1% KI (55% removal), 1% CaCl₂ (30% removal), and untreated pumice (3% removal).

3.4.5.4 Silica

The free energy of formation of mercury silicate has been estimated [80,81]. An equilibrium analysis of the mercury-silica chemical reaction in a simulated flue gas matrix has been calculated [80]. The simulation shows that in the absence of chlorine or sulfur, mercury silicate, HgSiO₃, is the favored equilibrium product over a temperature range of 440 - 620°F [80]. The effect of chlorine and sulfur, at levels found in typical coals, is to suppress the formation of mercury silicate in favor of mercuric chloride and mercuric sulfate [80].

3.4.5.5 Fly Ashes

The utilization of fly ash as a sorbent is highly desirable because it is an unwanted and voluminous waste product of combustion processes, often presenting disposal problems. One hundred million tons of coal fly ash are produced each year in the United States [78]. The composition of fly ashes is highly variable. Fly ash will be composed of SiO₂ and Al₂O₃, as well as lesser amounts of other oxides and unburned carbon. The composition of fly ash will depend upon the coal and the utility process conditions. For example, the major oxides found in a Wilcox east-central Texas lignite ash, would be, in order of decreasing weight, SiO₂, Al₂O₃, CaO, Fe₂O₃, MgO, TiO₂, K₂O, and Na₂O [75].

Some fly ashes have been demonstrated to oxidize elemental mercury, thereby making it easier to capture in flue gas desulfurization scrubber solutions [69,76,77]. Radian has oxidized elemental mercury by using a fixed bed of fly ash and sand [77]. The oxidation of elemental mercury could be occurring because of the presence of catalytic oxides such as vanadium pentoxide. Other fly ashes have been shown to adsorb elemental mercury, possibly because of the unburned carbon [69]. It is not a simple matter to determine the mechanism of fly ash oxidation or adsorption of mercury because of its highly variable and complex composition.

4.0 ECONOMIC CONSIDERATIONS

The last 1997 price of mercury is \$ 187/flask [50]. A flask contains 76 pounds of mercury. A 500 MW_e power plant will emit on the order of three flasks of mercury per year. Therefore, the removal of mercury from flue gas would be done to comply with future environmental regulations and not to generate a profit from the possible recovery of mercury. A comparison of potential sorbents is given in Table 8. The sorbent capacities are usually low. Sorbent capacities reported in the literature are typically on the order of 100 micrograms Hg/gram sorbent. Therefore, a high sorbent/mercury ratio, often on the order of 3000:1 [14], is needed to achieve a high percentage of mercury removal. Gold has the most attractive physical attributes, namely its inertness (few poisons/interferents, namely H₂S), the ability to sorb many mercury species, and its complete regenerability. These properties make gold an outstanding sorbent for analytical systems in the determination of total (elemental and oxidized) mercury.

Unfortunately, gold is the most expensive sorbent on a per kg basis, and may be impractical for use in large-scale flue gas clean up. Silver has similar characteristics to gold and is far cheaper. However, silver is a poor sorbent for some oxidized forms of mercury such as dimethyl and diethyl mercury. Silver is also less inert and will form an oxide. High surface area gold, deposited on a ceramic monolith support, possesses a much larger capacity for mercury. Roberts recently reported the capacity of gold supported on the ADA monolith as 0.1 gram Hg/gram Au [68]. This greatly improves the economic viability of gold sorbents. Activated carbons are the most studied mercury sorbents. Activated carbons have some serious drawbacks, including high cost, poor utilization/selectivity for mercury, and limited regenerability. Activated carbons are often promoted with halogens or sulfur to improve their ability to sorb elemental mercury. This improvement comes at a price; promoted activated carbons are three times more costly than unpromoted carbons.

Vanadium pentoxide is listed in Table 8 as a high temperature (1000°F) sorbent. It is likely that the capacity of a vanadium pentoxide sorbent for mercury in flue gas will be small. There are many binary vanadium oxides, such as the alkali vanadates, zinc vanadate, and cadmium vanadate. Other metals, such as zinc, cadmium, sodium, potassium, may compete with mercury for adsorption. Manganese dioxide is cheaper than activated carbons. The limited data [37,38] on manganese dioxide is promising, and suggests MnO_2 is a low temperature sorbent for both elemental and oxidized forms of mercury. Lime and sodium chloride are listed as promoters for the unburned carbon in fly ash. Both merit further examination because of their relatively low cost.

Table 8 Sorbent Cost

Sorbent	Regenerable	Cost, \$ per ton [50,51]	Capacity (10^{-6} g Hg/g)
Au	Completely	10,000,000	1 - 10 (on thin films)
$\text{Au}_{(\text{monolith})}$	Completely	100,000	
Ag	Completely	145,000	1 (on thin films)
V_2O_5		12,000	
PAC		3,000	50 - 17,000
AC	Few cycles	1,000	1 - 50
MnO_2		250	200
$\text{Ca}(\text{OH})_2$		75	
NaCl		30	

Table 9 Estimated Annual Cost of Sorbent in a 500 MW_e Power Plant

100 kg Hg emissions/year and a 3000:1 sorbent/Hg ratio

Sorbent	Initial Capital Cost of Regenerable Sorbent \$
Au	9,900,000 with daily regeneration
$\text{Au}_{\text{monolith}}$	200,000 with daily regeneration and a 10:1 sorbent/Hg ratio [67]
Ag	130,000 with daily regeneration
Sorbent	Annual Cost of Sorbent \$

PAC	990,000	without regeneration
AC	330,000	without regeneration
V ₂ O ₅	3,900,000	without regeneration
MnO ₂	82,500	without regeneration
Ca(OH) ₂	21,000	without regeneration
NaCl	8,400	without regeneration

Table 9 lists the estimated annual cost of the sorbent for a 500 MW_e power plant. The annual costs for the noble metal sorbents are exorbitant. The capacity of the noble metals for mercury is low. This fact coupled with the enormous initial sorbent expense means that noble metal sorbents would have to be frequently regenerated, entailing additional process expense. These factors suggest that traditional low surface area noble metal sorbents are not economically practical for large scale mercury flue gas clean-up. The advances in noble metal sorbent technology being developed by ADA may change this prognosis [31,68]. The annual sorbent costs for an activated carbon clean-up process are also high. A 3000:1 annual carbon:mercury ratio has been suggested as necessary to attain efficient removal of mercury [14]. A recent estimate of the cost of activated carbon for the removal of mercury from the flue gas of a 500 MW_e power plant has been given as \$ 500,000/year [14]. This is in good agreement with the estimate provided here. If a 50,000:1 carbon:mercury ratio is needed, as has been suggested by Chang [87], then the annual cost of activated carbon sorbent would be 17 times greater, around \$ 10,000,000/year.

It can be seen that the annual cost of a vanadium pentoxide sorbent is estimated to be very high. The real economic viability of a V₂O₅ sorbent may be somewhat better. The sorbent could be regenerable. A vanadium pentoxide sorbent could possibly do double duty as a SO_x oxidation catalyst. It can be concluded that an economically viable sorbent for the removal of mercury from flue gas could be either a base metal oxide or a halogen salt. The base metal oxide could be manganese dioxide, a lime-based, or a silicate-based sorbent. The halogen salt could be sodium chloride or calcium chloride. Possible sorbents that merit further research are discussed in the next section.

5.0 RECOMMENDATIONS FOR FUTURE SORBENT RESEARCH

It is suggested that future research concentrate on base metal oxide sorbents and halide sorbents because of their lower cost per ton versus activated carbon and noble metal sorbents. Fly ash, containing both unburned carbon and many metal oxides, should also be further studied as a potential sorbent. Development of improved methods of sorbent-flue gas contact merits

study. The ultimate fate of mercury removed by the sorbent also requires critical examination.

5.1 Near-Term Sorbent Candidates

Based upon the literature survey, it is believed that partially reducible multivalent metal oxides, fly ashes, halides, and activated carbons represent the best candidates for short-term development work.

5.1.1 Partially Reducible Base Metal Oxides

Partially reducible oxides such as manganese dioxide, hopcalite, and vanadium pentoxide have been demonstrated to act as mercury sorbents. Many base metal oxides are known to react with mercury species to form binary mercury oxides.

The relationship between oxide reducibility and capacity needs to be examined. Many deductions about oxide sorbents can be made if it is assumed that these sorbents form a binary (or ternary) oxide with mercury.

Catalysts for the partial oxidation of hydrocarbons such as manganese dioxide and vanadium pentoxide have been demonstrated to sorb mercury. It is suggested that other partially oxidation catalyst oxides such as Bi_2O_3 , $(\text{Bi}_2\text{O}_3)_{0.75}-(\text{Y}_2\text{O}_3)_{0.25}$, MoO_3 , and $3\text{MoO}_3\text{-Fe}_2(\text{MoO}_4)_3$ will also sorb mercury. These oxides share several important characteristics with manganese dioxide and vanadium pentoxide, such as:

- 1) Containing multivalent metal cations
- 2) Possessing many lower oxides
- 3) Being reduced to a lower oxide (as opposed to metal) in methane, and
- 4) Oxidizing hydrocarbons via a Mars-Maessen mechanism

It is proposed that metal oxides which are partial oxidation catalysts for hydrocarbon oxidations, such as the oxidation of methanol to formaldehyde, would be effective mercury sorbents at temperatures of 68 - 750°F. It is also proposed that the oxides of metals that do not amalgamate with elemental mercury, i.e., the oxides of iron, niobium, vanadium, molybdenum, tantalum, and tungsten, are potential mercury sorbents. In this case, the bare metal does not adsorb-amalgamate with mercury, and the oxide phase can act as a sorbent, rather than as a poison.

5.1.2 Fly Ashes

Some fly ashes have been shown to adsorb mercury [69]. This is probably due to the presence of unburned carbon. The use of fly ash as a sorbent for mercury removal from flue gas would provide a welcome use for an unwanted waste material.

5.1.3 Halides

Most metal halides are known to react with mercuric chloride to form a double salt. Halide salt promoted inert mineral substrates have also been demonstrated to remove elemental mercury from nitrogen. Salts such as sodium chloride and calcium chloride merit further study because of their low cost.

5.1.4 Activated Carbons

Activated carbons are the most studied sorbents, and are the commercial sorbent for waste incinerators. The development of lower cost activated carbons is needed. The regenerability of activated carbons needs improvement. The issue of long-term sequestration of mercury on spent, activated carbons has been neglected.

5.2 Long-Term Potential Sorbents

It is proposed that non-reducible insulator oxides, insulator oxides promoted with halides, and noble metal monoliths are viable candidates for longer-term research.

5.2.1 Non-Reducible Oxides

The non-reducible oxides are the insulator minerals such as alumina, silica, aluminosilicates, and lime. Unpromoted, these have been demonstrated to be poor sorbents for mercury. It is speculated that at very high temperatures these inert oxides will exhibit activity as mercury sorbents via chemical reaction. This is analogous to the catalytic behavior of inert oxides for the oxidative coupling of methane at high temperatures [49].

A three-way correlation between oxide reducibility in methane, sorbent capacity-activity, and behavior as a hydrocarbon catalyst may be discovered. It is hypothesized that oxides which are catalysts for the partial oxidation of hydrocarbons, would be active sorbents for elemental mercury. These oxides are readily reduced to a lower oxide. It is speculated that oxides which are catalysts for the oxidative coupling of methane to ethane, would show activity for the sorption of elemental mercury at elevated ($\sim 1300^{\circ}\text{F}$) temperatures. These oxides are difficult to reduce. Deep oxidation catalyst oxides such as NiO are hypothesized to be inactive mercury sorbents. These oxides are readily reduced to a metal phase, and do not possess stable lower oxides. The underlying assumption is that one route for oxide sorbents to capture elemental mercury is to first oxidize it, possibly via lattice oxygen, and then form a binary or ternary metal oxide with mercury. This is our proposed mechanism for the action of MnO_2 and V_2O_5 sorbents.

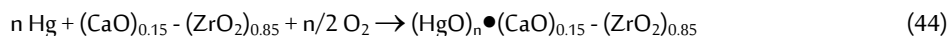
Most of the double oxides of mercury such as $11\text{MnO}_2 \bullet \text{HgO}$, $\text{V}_2\text{O}_5 \bullet \text{HgO}$, $\text{MoO}_3 \bullet \text{HgO}$, etc., are thermodynamically stable:

$$\Delta G_{\text{f double oxide}} = n (\Delta G_{\text{f oxide 1}}) + \Delta G_{\text{f HgO}} + \Delta G_{\text{rxn}} \quad (40)$$

where ΔG_{rxn} is the free energy of reaction and n is the number of moles of oxide sorbent present in the binary oxide. ΔG_{rxn} will be small in comparison to the sum of $\Delta G_{\text{f oxide}}$ and $\Delta G_{\text{f HgO}}$ for the insulator metal oxides such as silica and alumina. For example, the free energy of formation of magnesium silicate, $\text{MgO} \bullet \text{SiO}_2$, is approximately equal to the sum of the free energies of formation of magnesium oxide and silica. There are thousands of such stable binary and ternary oxide minerals, such as aluminates, silicates, aluminosilicates, chromates, and vanadates. The free energies of formation of most postulated binary and ternary oxides of mercury will be negative and large. However, the free energy of reaction between mercury (or mercuric chloride), oxygen, and the oxide sorbent will be small, and possibly positive. In addition, the kinetics of these reactions requires examination. There are electronic and/or steric factors that inhibit many, if not most, potential reactions between oxides and mercury.

The mechanism for mercury capture at elevated temperatures of $1300 - 2700^{\circ}\text{F}$ by non-reducible oxide sorbents could be illustrated by these chemical reactions:





There is evidence to suggest the existence of mercury aluminate, silicate, and aluminosilicate glasses and compounds. Zinc crown glasses, which are composed primarily of silica, zinc oxide, and alumina, are commercially available [61]. There are many naturally occurring zinc minerals such as willemite Zn_2SiO_4 , hemimorphite $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \bullet \text{H}_2\text{O}$, gahnite ZnAl_2O_4 , and franklinite ZnFe_2O_4 [59]. The silicates cadmium orthosilicate, Cd_2SiO_4 , and cadmium metasilicate, CdSiO_3 , can be made by fusing finely powdered cadmium oxide and quartz at 2200°F [46]. Zinc, cadmium, and mercury are in the same chemical family. The compounds HgAl_2S_4 , HgAl_2Se_4 , and HgAlTe_4 are known defect chalcopyrite structured semiconductors [59]. These compounds are isomorphic with HgAl_2O_4 ; oxygen is in the same chemical family as sulfur, selenium, and tellurium. Once formed, these compounds should be highly stable. A high reaction temperature, on the order of 2000°F , is proposed because of the stability of alumina and silica. The simulations of Owens and Biswas [80,81] suggest a lower reaction temperature of 500°F .

Calcium stabilized zirconia is suggested as a possible sorbent because of its mobile oxygen anions at mildly elevated temperatures of 570°F and above. Calcium stabilized zirconia is an oxygen-conducting solid electrolyte. The mobile oxygen anions could serve to oxidize/capture mercury at lower temperatures than alumina, silica, and aluminosilicates.

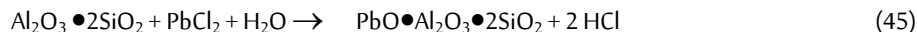
5.2.2 Non-Reducible Oxides Promoted With Halides

Ash from coal and municipal waste combustion contains alumina, silica, and aluminosilicates. However, most of the mercury originally present in coal or municipal solid waste ends up in the flue gas [6,74]. Indirect evidence [57,58] suggests that the halides HCl , NaCl , and HgCl_2 could act as catalysts/reagents for the formation of stable mercury double and ternary oxides with alumina and silica. The data on cadmium silicates [46], indicating formation at 2200°F by reaction between cadmium oxide and quartz, suggests that mercury aluminates, silicates, and aluminosilicates could form by solid state reaction between mercuric oxide, alumina, and silica at very high ($\sim 2200^\circ\text{F}$) temperatures. Equilibrium calculations indicate that elemental mercury and mercuric chloride are the dominant mercury species in flue gas; mercuric oxide will exist in flue gas as a tiny proportion of the total mercury [69]. Halides such as salts and hydrochloric acid could serve to:

- 1) reduce the reaction temperature (from circa 2200 to 1300°F) needed to form stable mercury aluminosilicate

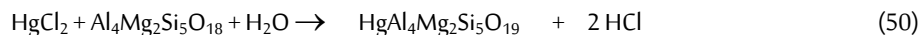
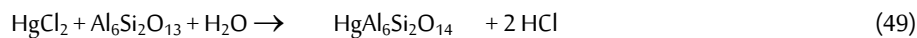
compounds.

- 2) allow mercuric chloride or elemental mercury to react with alumina, silica, or aluminosilicate sorbent, possibly eliminating a need for an unstable mercuric oxide intermediary. Shadman and Uberoi [57] report that metakaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, can react with lead chloride in flue gas viz:



The lead aluminosilicate compound $\text{PbAl}_2\text{Si}_2\text{O}_8$ was detected via x-ray diffraction. Kaolinite and bauxite were reported to remove 80% of the lead in a simulated flue gas. Emathlite, alumina, and silica removed 50%-60% of the lead. The sorbents were at 1290°F, and lead was supplied as PbCl_2 in a simulated flue gas matrix of 15% CO_2 , 3% O_2 , 80% N_2 , and 2% H_2O . Although SiO_2 and Al_2O_3 alone are good for lead removal, the combined presence greatly enhances the overall capacity for lead removal. Most of the lead captured was found to be water insoluble [57].

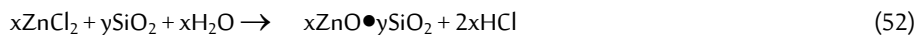
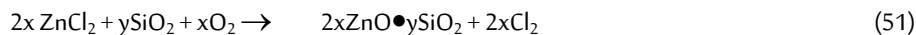
Similarly, it is possible that mercuric chloride can participate in the reactions:



Reactions (47) and (48) involve the common refractory materials mullite and cordierite.

Jakob, Stucki, and Struis [58] examined the thermal evaporation of cadmium, copper, lead, and zinc from synthetic fly ashes. Jakob et al [58] found evidence that zinc chloride can react with silica, alumina, aluminosilicates, and sodium aluminosilicate.

They propose that the following reactions can occur between zinc chloride and silica [58]:



In addition, they propose that the addition of sodium chloride to the synthetic fly ash promotes the formation of metal chlorides, which, in turn, promotes the incorporation of metals such as zinc into ash [58]. Zinc and mercury are in the same chemical family, and possess some similar chemical properties. However, the simulations of Owens and Biswas suggest that halogens retard the formation of mercury silicate [80,81].

5.2.3 Noble Metal Monoliths

Gold possesses the best regenerability of all the sorbents. Gold will remove both elemental and oxidized forms of mercury. The problem with gold sorbents has been their low capacity and high initial capital cost. The research by ADA on gold monoliths is making progress in both of these areas [31,68].

5.3 Long-Term Sequestration

Little research has been done on the long-term stability of spent sorbents. It is important to determine the ultimate fate of mercury after it is removed by a sorbent. If the spent form of a sorbent is not stable, then mercury could off-gas or leach back into the environment. Many mercury compounds, such as the iodides, are light-sensitive. The effect of temperature, moisture, ultraviolet radiation, and visible radiation on the sequestration of mercury requires further examination to determine the safe ultimate disposal of spent sorbents.

5.4 Contacting Method

One of the main factors limiting the removal of mercury from flue gas is the method of contacting the flue gas with the sorbent. The number of collisions between mercury and the sorbent is determined in part by the flue gas residence time with the sorbent,

mercury concentration in the flue gas, flue gas temperature, and mixing between the sorbent and gas, i.e., reactor design. Devising improved means of contacting the sorbent with the flue gas may be almost as important as the development of better sorbents. Depending on its thermal stability, it may be advantageous to add the sorbent to coal, municipal solid waste, or medical waste before combustion to increase sorbent-flue gas contact. Recycle reactors offer increased flue gas-sorbent contact compared to a single pass packed bed and could simulate the effects of increased residence time on a bench-scale. A comparison of the economics of sorbent-coal firing versus sorbent introduction via spray driers or duct injection requires investigation.

DISCLAIMER

References in this paper to any specific commercial product, process, or service are to facilitate understanding, and does not necessarily imply its endorsement by the United States Department of Energy.

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