

Mercury in coal and the impact of coal quality on mercury emissions from combustion systems

Allan Kolker ^{a,*}, Constance L. Senior ^b, Jeffrey C. Quick ^c

^a US Geological Survey, Eastern Energy Resources Team, 956 National Center, Reston, VA 20192, USA

^b Reaction Engineering International, 77 W. 200 South, Salt Lake City, UT 84101, USA

^c Utah Geological Survey, P.O. Box 146100, Salt Lake City, UT 84114-6100, USA

Available online 29 September 2006

Abstract

The proportion of Hg in coal feedstock that is emitted by stack gases of utility power stations is a complex function of coal chemistry and properties, combustion conditions, and the positioning and type of air pollution control devices employed. Mercury in bituminous coal is found primarily within Fe-sulfides, whereas lower rank coal tends to have a greater proportion of organic-bound Hg. Preparation of bituminous coal to reduce S generally reduces input Hg relative to in-ground concentrations, but the amount of this reduction varies according to the fraction of Hg in sulfides and the efficiency of sulfide removal. The mode of occurrence of Hg in coal does not directly affect the speciation of Hg in the combustion flue gas. However, other constituents in the coal, notably Cl and S, and the combustion characteristics of the coal, influence the species of Hg that are formed in the flue gas and enter air pollution control devices. The formation of gaseous oxidized Hg or particulate-bound Hg occurs post-combustion; these forms of Hg can be in part captured in the air pollution control devices that exist on coal-fired boilers, without modification. For a given coal type, the capture efficiency of Hg by pollution control systems varies according to type of device and the conditions of its deployment. For bituminous coal, on average, more than 60% of Hg in flue gas is captured by fabric filter (FF) and flue-gas desulfurization (FGD) systems. Key variables affecting performance for Hg control include Cl and S content of the coal, the positioning (hot side vs. cold side) of the system, and the amount of unburned C in coal ash. Knowledge of coal quality parameters and their effect on the performance of air pollution control devices allows optimization of Hg capture co-benefit.

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1. Introduction

According to the US Environmental Protection Agency's Information Collection Request (ICR) compilation (USEPA, 2002), 48 T of Hg, or about 64% of Hg input to the boiler, was emitted from US

coal-burning utility power stations in 1999. With the adoption of recent USEPA rules, plans are now in place to limit Hg emissions from USA coal-fired utilities, the largest remaining point-source category of emissions not currently regulated. The Clean Air Interstate Rule or CAIR (USEPA, 2005a) specifies reductions in NO_x and SO₂ emissions that are projected to result in a 40% reduction in Hg emissions in the utility sector by 2010. This Hg reduction will largely be accomplished with existing technologies,

* Corresponding author. Tel.: +1 703 648 6418; fax: +1 703 648 6419.

E-mail address: akolker@usgs.gov (A. Kolker).

primarily as a co-benefit of reducing other pollutants such as NO_x and SO₂, in 28 eastern states and the District of Columbia. A similar plan has been introduced in Canada, with 2010 emissions caps that differ by province, and the possibility of more stringent reductions by 2018 (CCME, 2005).

Ultimately, Hg-specific technology will be required in the USA to achieve a 70% reduction in Hg emissions by 2018 under the Clean Air Mercury Rule or CAMR (USEPA, 2005b). Sorbent injection approaches to Hg reduction having optimal Hg capture efficiencies of 70–90% at the pilot scale (Pavlish et al., 2003), appear promising in achieving these reductions. Similar optimal removals have been achieved in recent full scale demonstrations (Thompson et al., 2005). The effect of added sorbents on the suitability of coal combustion by-products for use in commercial applications is of concern to industries that utilize these materials. While Hg-specific control technology continues to develop rapidly, reducing Hg loading and increasing capture efficiency by existing air pollution control devices are more immediate concerns. This paper presents relevant information on Hg concentration and distribution in coal and reviews factors that influence Hg capture by existing air pollution control devices.

2. Mercury in coal

2.1. Concentration ranges and basis for comparison of mercury in coal

Mercury contents of coal differ by coal basin, by rank, and within individual coal beds, reflecting diagenetic, coalification, and post-diagenetic differences at all scales. Mercury concentrations exceeding 1 mg/kg are rare and generally result from mineralization that post-dates coal formation (Finkelman, 2003; Diehl et al., 2004; Brownfield et al., 2005). The average Hg concentration of coal delivered to USA power stations in 1999 is 0.10 mg/kg (USEPA, 2002; Quick et al., 2003). This average is substantially lower than the USA average (0.17 mg/kg) for over 7000 coal samples in the US Geological Survey (USGS) COALQUAL database, which is based on in-ground Hg concentration (Finkelman, 1993; Bragg et al., 1998). This difference primarily reflects (1) the fact that coal preparation, used to reduce S contents of some eastern coal, generally reduces Hg relative to in-ground values; and (2) increased use of USA western coal having lower Hg concentrations

relative to the in-ground average expressed in the COALQUAL database.

Information on Hg concentration of commercial coal is available for a number of other countries. In Canada, a utility monitoring program conducted from 2002 to 2004 provided information on Hg input and emissions nationwide (Goodarzi, 2002; CCME, 2005). Assessment of Hg releases from the Russian Federation (ACAP, 2005) includes data on Hg in mine output of the major coal basins, summarized from available analyses. A weighted average of 0.08 mg/kg is calculated, strongly controlled by results for the Kuznetsk basin, which accounts for about half of the coal extracted in Russia. Trace element data, including Hg, are being compiled for samples collected from about 60 coal-producing countries under the USGS World Coal Quality Inventory (Tewalt et al., 2005). Surveys of the Chinese coal industry have been conducted to assess the input of Hg from coal to combustion sources (Belkin et al., 2005; Streets et al., 2005). An arithmetic mean Hg concentration of 0.15 mg/kg was determined by Belkin et al. (2005) for 305 coal samples representing the output from mines in the major coal-producing regions of China. This study, and similar estimates, suggest that a lack of emissions controls in utility power stations, rather than a higher average Hg concentration, is primarily responsible for a per-ton Hg emissions rate in China that is roughly three times higher than that for USA utilities (Belkin et al., 2005). This output rate, combined with the largest coal production/consumption rates in the world, make China the world's largest emitter of Hg to the atmosphere.

Mercury concentrations alone are not a sufficient basis for comparison of different coal samples because moisture and calorific values vary considerably by rank. Low-rank coal can have moisture contents in excess of 30%, whereas moisture in bituminous coal is typically 1–5%. The large difference in moisture between low-rank and higher rank coal makes it difficult to compare weight concentrations unless they are taken on an equivalent dry basis. Comparison by concentration alone underestimates Hg loading by low-rank coal such as lignite, because a greater mass of lignite must be used to generate equivalent energy, compared to bituminous coal. For this reason, the USEPA (2005c) uses an energy equivalent basis in limits for Hg emitted from small non-utility boilers, and will adopt a similar approach for utilities under CAMR and CAIR. Comparison of Hg contents on an energy equivalent basis is advocated by Toole-O'Neil et al. (1999).

2.2. Mercury modes of occurrence in coal

An understanding of the mode of occurrence of Hg in various USA coal samples has been attained primarily through a combination of selective chemical leaching studies (Palmer et al., 1998, 2002), and direct determinations of coal constituents using methods such as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS; Diehl et al., 2004; Kolker et al., 2002). In bituminous coal, Fe-sulfides (pyrite and marcasite) are commonly the primary hosts of Hg, whereas the proportion of organic-hosted Hg is generally greater in lignite and subbituminous coal.

Mercury concentrations in pyrite, and the proportion of Hg in pyrite relative to other minor/trace elements, vary according to the timing of pyrite formation, and differences in the chemistry of fluids giving rise to enrichment in these elements. Limited grain-scale determinations of Hg in pyrite (Fig. 1) indicate concentrations in the mg/kg range, corresponding to enrichment factors as great as 100 or more, relative to whole-coal Hg concentrations (Diehl et al., 2004; Kolker et al., 2002). In the Warrior coalfield of northwestern Alabama, pyrite framboids that accompany coal formation have Hg concentrations <1 mg/kg, whereas late stage vein-

filling pyrite has average Hg concentrations of about 20 mg/kg (Diehl et al., 2004). A similar trend was found for a West Virginia coal sample (Fig. 1), in which framboidal pyrite is less Hg-enriched than other forms of pyrite in this sample. This finding is potentially favorable from a coal preparation standpoint, because framboidal pyrite is difficult to remove by coal preparation (see Section 2.3). In coal that contains both pyrite and marcasite, there can be a considerable difference in Hg concentration (Robertson, 2000). Because the concentration of Hg in pyrite can be quite variable, basin-scale correlation between Hg and pyritic S generally yields considerable scatter, whereas better correlations between these parameters are found within coal beds or portions of beds.

Organically bound Hg is the next most abundant form of Hg in bituminous coal, and the most abundant form overall in some low-rank coal. Direct determinations of Hg concentrations in organic matter in coal are very limited. Using LA-ICP-MS, Diehl et al. (2004) showed that the concentrations of Hg and associated elements in pyrite were an order of magnitude higher than those in organic parts of coal from three mines in the Warrior coalfield. An organic association for Hg in coal is also inferred by the difference between whole coal values and the sum of selective leaching results for Hg in mineral matter.

In atypical Hg-rich coal (i.e., ≥ 5 mg/kg), compounds such as HgS (cinnabar), HgSe (tiemannite), and even native Hg have been reported (Brownfield et al., 2005). In Hg-rich coal, concentrations are sufficient to allow speciation determinations by X-ray absorption near-edge structure (Brownfield et al., 2005), as used for other elements present at mg/kg concentrations (Huggins et al., 2002). In coal with more typical (sub-mg/kg) Hg concentration, a small portion of the Hg may be in solid solution in PbSe, a common trace mineral (Hower and Robertson, 2003).

2.3. Mercury reduction by coal preparation and selective mining

Coal preparation is effective in achieving modest Hg reductions in eastern USA bituminous coal by reducing pyrite contents (Toole-O'Neil et al., 1999; Pavlish et al., 2003). Various processes are used, including coal washing, and more advanced techniques such as froth flotation, selective agglomeration, cyclones, and chemical approaches. Coal

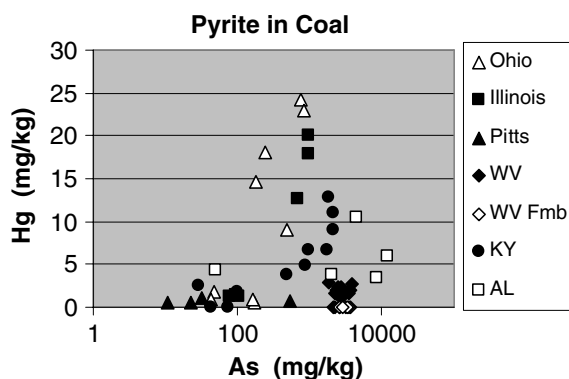


Fig. 1. Plot of Hg concentration in pyrite (in mg/kg) as a function of As concentration, based on reconnaissance laser ablation (LA) ICP-MS analysis of 6 USA eastern bituminous coals (data from Diehl et al., 2005; Kolker et al., 2002). Data points represent individual LA-ICP-MS spot analyses (analysis spot ranges in size from 10 to 50 μ m). Samples include an Ohio 5/6/7 blend (Ohio; whole coal = 0.18 mg/kg Hg), Illinois #6 (Illinois; 0.06 mg/kg Hg), Pittsburgh (Pitts; 0.09 mg/kg Hg), and coals from the Black Warrior Basin of Alabama (AL), the Upper Coalburg Coal from West Virginia (WV), and an eastern Kentucky coal (KY). Framboidal pyrite in the WV sample is indicated in the legend as WV Fmb. Note log scale for As concentration.

preparation is primarily intended to reduce S contents and mineral matter; therefore, when Hg reduction is achieved it is obtained as a co-benefit to these primary goals. For bituminous coal, the amount of Hg reduction is highly variable, ranging from about 10% to as much as 70%, with an average of approximately 30% on an energy equivalent basis (Toole-O'Neil et al., 1999). The amount of reduction depends on the amount of pyrite present, Hg concentration in pyrite, proportion of the total Hg in pyrite, and the effectiveness of pyrite removal by the preparation process. Where Hg is principally in an organic association, as in much low-rank coal, it is unlikely that significant reduction of Hg can be achieved by coal washing. Rejection of the coarse pyritic fraction by pulverizers at the power plant reduces Hg input to the boiler regardless of whether the coal has been cleaned (Hower et al., 2005). These pulverizer rejects can account for a disproportionate fraction of Hg and their removal increases boiler performance as well as decreases S and Hg emissions.

In cases where Hg concentrations of coal beds are structurally or stratigraphically controlled, selective mining can be a useful approach to limiting the Hg concentration of delivered coal by avoiding the most Hg-rich zones or stratigraphic intervals (Sakulpitakphon et al., 2004; Diehl et al., 2004; Hower et al., 2005). This approach generally requires sampling and analysis at a level of detail beyond that ordinarily required of coal providers. Depending on economic factors of mining and specifications of utility coal contracts, the approach may or may not be cost effective.

3. Impact of coal quality on mercury removal in combustion systems

3.1. Coal properties, mercury speciation, and transformations in the boiler

Flue gas from coal combustion may contain gaseous elemental Hg (Hg^0) and gaseous forms of oxidized Hg, for example, mercuric chloride (HgCl_2), mercuric oxide (HgO), mercuric sulfate (HgSO_4), and mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$). Each of these species has different properties that determine its solubility in water and its potential for adsorption onto solid surfaces. Available measurement techniques only allow for the routine measurement of oxidized Hg (Hg^{2+}), particulate-bound Hg (Hg_p), and Hg^0 in flue gas. The determination of these three forms of Hg in flue gas is called the speciation of Hg.

Mercury exists as Hg^0 in the high temperature (~ 1600 K) regions of coal-fired boilers, irrespective of the form of Hg in the fuel. As the flue gas is rapidly cooled to temperatures in the range of 400–500 K, a series of complex reactions converts Hg^0 to Hg^{2+} and Hg_p , which are more readily captured than Hg^0 (see Section 3.2). Bench-, pilot-, and full-scale combustion research have produced theoretical models attempting to explain the speciation and capture of Hg in coal-combustion flue gases. Transformation of Hg^0 to Hg^{2+} involves both gas-phase (homogeneous) reactions (Edwards et al., 2001; Niksa et al., 2001; Qiu et al., 2003; Senior et al., 2002) and gas-solid (heterogeneous) reactions (Olson et al., 2003, 2005; Schofield, 2004).

As a result of chemical transformations in the flue gas, Hg enters the flue gas cleaning device(s) as a mixture of Hg_p , Hg^{2+} , and Hg^0 . In the presence of Cl, gas-phase equilibrium conditions favor the formation of HgCl_2 at flue gas cleaning temperatures. However, the oxidation of Hg^0 is kinetically limited by the homogeneous and heterogeneous reaction rates (Senior et al., 2002). Sulfur (as SO_2) reduces the homogeneous oxidation of Hg in flue gas (Qiu et al., 2003); S (as SO_2 and/or SO_3) can inhibit the sorption and oxidation of Hg^0 by carbon surfaces (Olson et al., 2003). Carbon surfaces, such as unburned C in fly ash, appear to be critical to several heterogeneous pathways for Hg oxidation. Unburned C in fly ash depends on the specific combustion system and the coal rank, with bituminous coal producing more unburned C than subbituminous or lignite coal in industrial and utility boilers. The most important factors that affect Hg transformations related to coal properties are coal rank, coal Cl concentration and coal S concentration.

3.2. Mercury capture in air pollution control devices

The extent of conversion of Hg^0 to Hg^{2+} and Hg_p depends on the flue gas composition, the amount and properties of fly ash and the flue gas quench rate. These factors are, in turn, dependent on the type (and properties) of coal, the combustion conditions, the design of the boiler and downstream heat extraction equipment, and the air pollution control devices (APCDs).

The most common APCDs in USA coal-fired utility power stations include: (1) electrostatic precipitators (ESPs), used with or without flue-gas desulfurization (FGD) controls (Fig. 2), and (2) fabric filters (FFs), which may be used alone or with

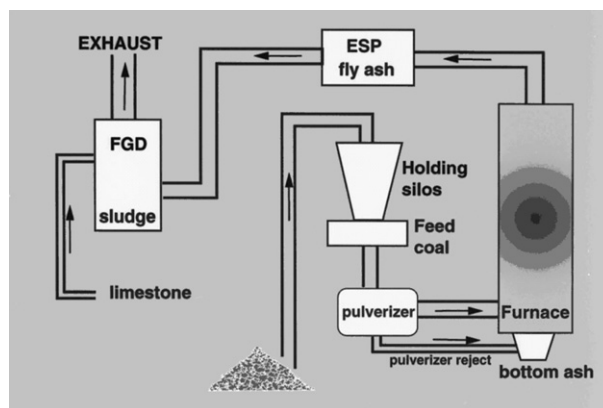


Fig. 2. Schematic showing flow of materials in a coal-fired boiler equipped with electrostatic precipitator (ESP) and flue-gas desulfurization (FGD) air pollution control devices. A portion of the Hg in feed coal is trapped in fly ash, bottom ash (which generally includes pulverizer rejects), and in FGD sludge.

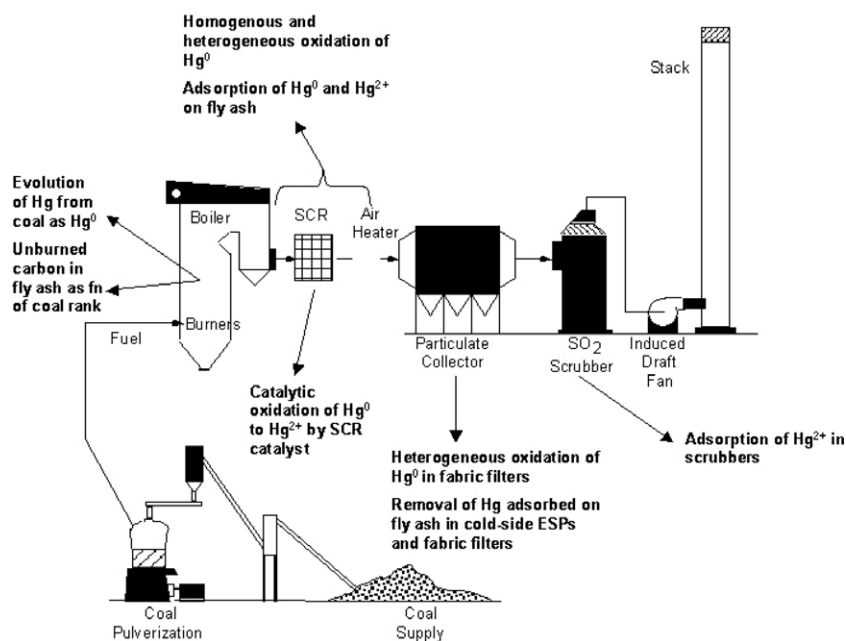


Fig. 3. Diagram of a coal-fired power plant, illustrating critical pathways for Hg transformations. Example shows use of selective catalytic reduction (SCR) and placement of particulate collector (fabric filter or electrostatic precipitator) on downstream (cold) side of air pre-heater (air heater).

spray dry adsorbents (SDAs). These control devices are designed to remove particulates (FFs, ESPs) or S (FGDs, SDAs) from flue gases. The position of an ESP relative to the air pre-heater device, downstream of the boiler, is an important distinction. Cold-side ESPs are installed downstream of the air pre-heater (Fig. 3), whereas hot-side ESPs are installed upstream of the air pre-heater, closer to the boiler.

The amount of Hg removed by an APCD depends on its type and the rank of coal being

burned. Empirical results (Kilgroe et al., 2002) show most efficient Hg removal for bituminous coal (>60%) in FF/SDA and FGD devices (Fig. 4). By contrast, cold-side ESPs (CESPs) remove only 40% of Hg from flue gases, and hot-side ESPs (HESPs) have virtually no effect on the pollutant. At plants burning subbituminous coal or lignite, APCDs are much less capable of removing Hg. For the former fuel, only FFs (60%) and FGD systems (15%) have exhibited much effectiveness. In the case

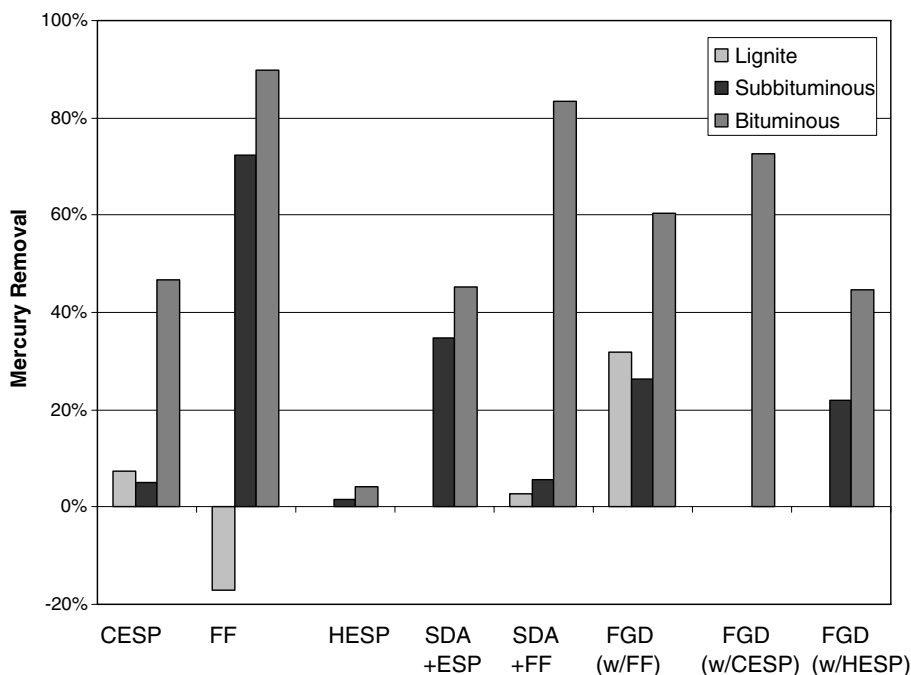


Fig. 4. Average Hg removal across APCDs in coal-fired utility boilers from EPA Information Collection Request (Kilgroe et al., 2002).

of lignite-burning plants, the removal of Hg is very low, in some cases apparently negative. Mercury removal is calculated from measurement of Hg in the flue gas at the inlet and outlet of the particulate control device. When little Hg is removed, limitations on the accuracy of the inlet and outlet measurements may result in apparent negative removals.

Equations describing the Hg removal behavior of these devices as a function of coal quality parameters, have been fit to the ICR data; these results were compared and evaluated by Quick et al. (2005).

3.2.1. Unburned carbon and mercury capture by fly ash

Heterogeneous reactions involve adsorption and desorption that lead to the adsorption of gas-phase Hg onto solid particles (Hg_p) and the formation of Hg^{2+} . A multi-step heterogeneous model has been proposed by researchers at the University of North Dakota – Energy and Environmental Research Center to characterize the adsorption and oxidation of Hg by activated C (Olson et al., 2003, 2005). The active sites are postulated to be C sites that act as Lewis bases. Oxidized Hg in the flue gas (Hg^{2+}) can bind to these sites. Acid gases (HCl, SO_2 , SO_3) also bind to these sites. HCl bound to a C site is postulated to adsorb elemental Hg from the gas; oxidants

in the gas (O_2 , NO_2 , NO) subsequently oxidize the Hg to Hg^{2+} , which can stay bound to the C or desorb, primarily as $HgCl_2$. Sulfur species (SO_2 , SO_3) compete for the basic sites and can inhibit the binding of Hg to the sites.

Adsorption of gas-phase Hg by unburned C and its capture in fly ash is an important process whereby Hg is trapped in particulate control devices. Often a consequence of low- NO_x burners or low- NO_x combustion systems, pulverized-coal boilers burning bituminous coal can produce high levels of unburned C, 5–30 wt.% as loss on ignition (LOI). Mercury has been found to concentrate in the C-rich fraction of fly ash (Hassett and Eylands, 1999; Hower et al., 1999b, 2000a,b).

Bituminous coal-ash produced under CESP conditions exhibits a consistent trend of increasing Hg removal with unburned C content (LOI in Fig. 5, from Senior and Johnson, 2005). This trend suggests that a relationship exists between C in ash and Hg removal for plants burning bituminous coal in pulverized-coal-fired boilers with CESP. This relation appears to be independent of the Cl content of coal (Section 3.2.2).

Data from the plant with an HESP show uniformly lower Hg removal for a given percentage of LOI as compared to the data for the other pulver-

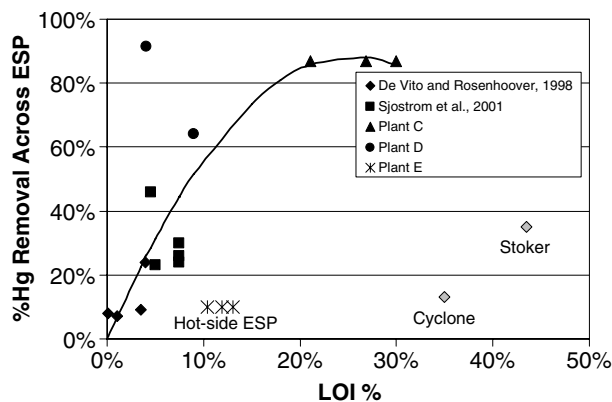


Fig. 5. Mercury removal across coal-fired boilers burning bituminous coal having an ESP (Senior and Johnson, 2005).

ized-coal-fired plants (Fig. 5). HESPs operate at temperatures of 300–400 °C, whereas CESPs operate at temperatures of 135–175 °C. Adsorption of Hg by fly ash or activated C has been observed to decrease as temperature increases (Karatza et al., 1996; Dunham et al., 2003). The higher temperatures of the HESP favor lower adsorption of Hg upstream of the ESP, and thus, less capture of particulate-bound Hg in the ESP. Furthermore, the flue gas path between the air pre-heater inlet and the inlet of a CESP provides additional residence time for Hg sorption, which may contribute to the higher removal of Hg observed for CESPs.

Values for Hg removal across CESPs in cyclone and stoker units are considerably lower than those for pulverized-coal-fired units having similar values of LOI (Fig. 5). For bituminous-coal fly-ash samples from pulverized-coal-fired boilers, the surface area of C present in the ash is between 40 and 100 m²/g C (Senior and Johnson, 2005), in agreement with values reported by Gao et al. (2002) for Class F (bituminous) fly-ash samples. The cyclone- and stoker-ash samples have much lower C surface areas (8–11 m²/g C), which may explain the lower percentage of Hg removal across ESPs in those boilers (Senior and Johnson, 2005).

Data from full-scale combustion systems show that Hg removal across ESPs in pulverized-coal-fired boilers burning bituminous coal appears to be related to the LOI or unburned C in the fly ash. The surface area of the C in the fly ash was remarkably consistent among the samples from pulverized-coal-fired units; combustion systems that produced fly ash with a lower C surface area showed lower Hg removal across the ESP. These conclusions cannot be extended to fly ash from subbituminous coal and

lignite, however. There is evidence in the literature (Gao et al., 2002; Senior and Johnson, 2005) that the surface area of C from Class C (subbituminous) fly-ash samples is considerably higher than that of Class F fly-ash samples on a per gram of C basis.

3.2.2. Effect of chlorine and other halogens

The halogen content of the coal affects oxidation of Hg in the flue gas by homogeneous, heterogeneous and catalytic pathways. Chlorine is the most significant halogen in combustion systems as far as Hg chemistry is concerned, but Br also plays a role in Hg oxidation.

The primary Hg oxidation product in flue gas is believed to be HgCl₂, the species favored by equilibrium conditions. The gas-phase transformation pathway involves the oxidation of Hg⁰ by atomic Cl. The concentration of Cl, in turn, depends on a complex series of gas-phase reactions involving O₂, water vapor, hydrocarbons, Cl compounds, and S compounds. A number of critical reactions limit the concentration of Cl and the subsequent conversion of Hg⁰ to HgCl and then to HgCl₂. Although NO₂ has been shown to oxidize Hg⁰ in laboratory experiments, it is not believed to play a major role in homogeneous Hg⁰ oxidation reactions, whereas SO₂ has been shown experimentally to affect Hg chemistry in gas-phase systems (Qiu et al., 2003).

The cooling rate in the flue gas has also been shown to strongly influence homogeneous oxidation of Hg⁰ (Senior et al., 2002). High flue-gas cooling rates between the air pre-heater inlet and air pollution control device inlet limit reaction rates associated with homogeneous oxidation reactions.

The combination of a selective catalytic reduction (SCR) system, used to reduce NO_x emissions,

and a wet FGD, used to reduce SO_2 emissions, can be an effective way to utilize existing APCDs for the control of Hg emissions from coal-fired power plants. Selective catalytic reduction systems have been observed to convert Hg^0 to Hg^{2+} in coal-fired power plants (Laudal, 2002; Richardson et al., 2002). The average of recent full-scale data for

plants firing bituminous coal was 72% oxidation, and the range of Hg oxidation observed was 30–98%. Limited data from plants burning subbituminous coal suggest much lower amounts of Hg oxidation across SCRs in these plants. Maximizing the amount of Hg^{2+} in the flue gas can enhance the performance of a wet FGD in removal of Hg. This

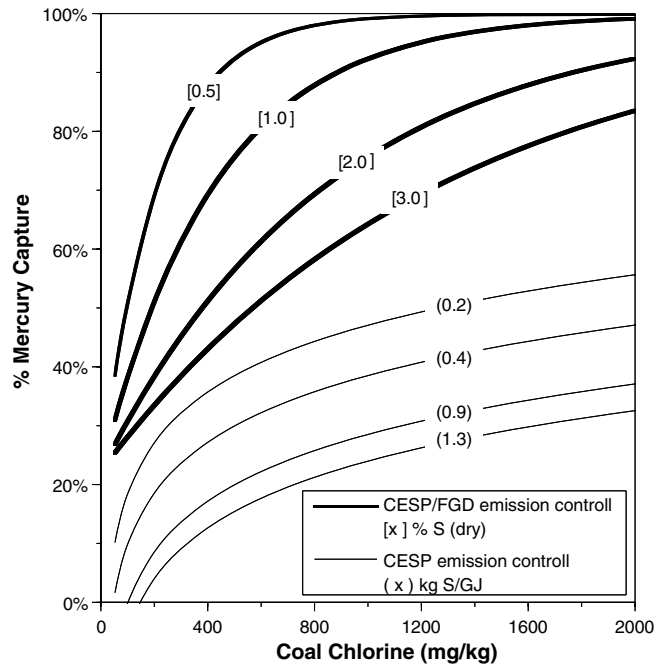


Fig. 6. Empirical equations predict decreasing Hg capture with increasing coal S for two common emission control systems used at USA power plants. Bold lines are for cold-side electrostatic precipitators with wet flue-gas desulfurization (CESP/FGD) based on an equation by SAIC (2003). Thin lines are for cold-side electrostatic precipitators (CESP) based on an equation from the Electric Power Research Institute (Quick, 2006).

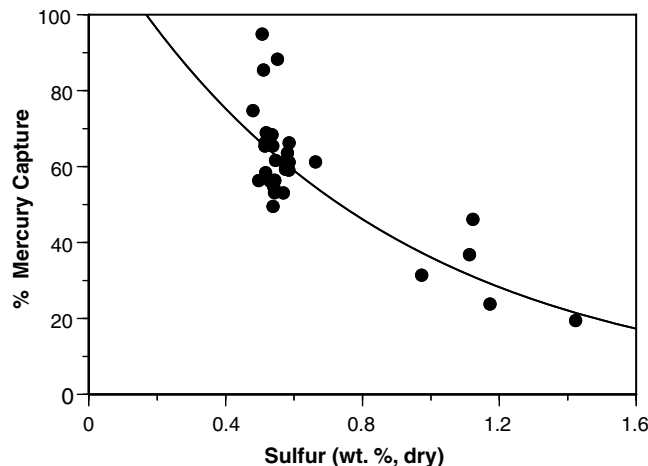


Fig. 7. Decreasing Hg capture with increasing coal S. Data points show weekly averages (CEA, 2004) observed for two units equipped with CESP emission controls where fly-ash C exceeds 5% (average 11%). Mercury capture was estimated after Meij et al. (2002) using coal and fly-ash Hg values.

offers a low-cost option for control of Hg from coal-fired power plants.

Laboratory-scale investigations of Hg chemistry across SCR catalysts are more limited, but much can be learned from the few that have been undertaken. Lee et al. (2004) observed adsorption and oxidation of Hg⁰ across a commercial SCR catalyst to depend on HCl content of simulated flue gas. In another study (Hocquel et al., 2001), elemental Hg was observed to oxidize across commercial SCR catalysts in simulated flue gas at typical SCR temperatures, with oxidation increasing as HCl content increased. Pilot-scale data on SCR catalysts using simulated flue gas and power plant flue gas also suggest higher Hg oxidation for flue gas from bituminous coal, which contains more HCl than that from lower rank coal (Richardson et al., 2002).

A kinetic model (Senior, 2006) based on the combination of mass transfer and heterogeneous catalysis was developed to predict the oxidation of Hg across SCR catalysts assuming that HCl in the flue gas was the agent for Hg oxidation. The model reproduced the variation of Hg oxidation with space velocity (i.e., gas residence time in the catalyst) and, without any catalyst parameter adjustment, predicted the Hg oxidation for two different coal blends, of differing Cl concentration, observed in a

slipstream reactor deployed at a coal-fired power plant (Spitznogle and Senior, 2005).

Until recently, the impact of other halogens in coal on Hg oxidation has been ignored. Bromine compounds react with Hg in the gas phase (Goodsite et al., 2004), however, the Br concentration of coal is considerably less than the Cl concentration, on the order of 1 mg/kg Br (or less) as compared to ~10–5000 mg/kg Cl. Vosteen et al. (2005) have demonstrated that the addition of Br to fuel or flue gas can have a significant effect on Hg speciation and on the partitioning of Hg between the gas and solid phases.

3.2.3. Sulfur

Empirical equations derived from measurements at 80 USA power plants (USEPA, 2002) predict decreasing Hg capture with increasing coal S (Fig. 6). Explanations of why S reduces Hg capture vary. Qiu et al. (2003) suggested that SO₂ scavenges free radicals in the flue gas (O and OH), which results in less Cl radical formation, and therefore, less gas-phase oxidation of Hg. Hocquel et al. (2001) suggested that S may simultaneously inhibit the conversion of flue-gas HCl to reactive Cl₂ by sulfation of catalytic metal-oxide surfaces, and promote the gas-phase reduction of Cl to less-reactive HCl and by-product SO₃; both reactions

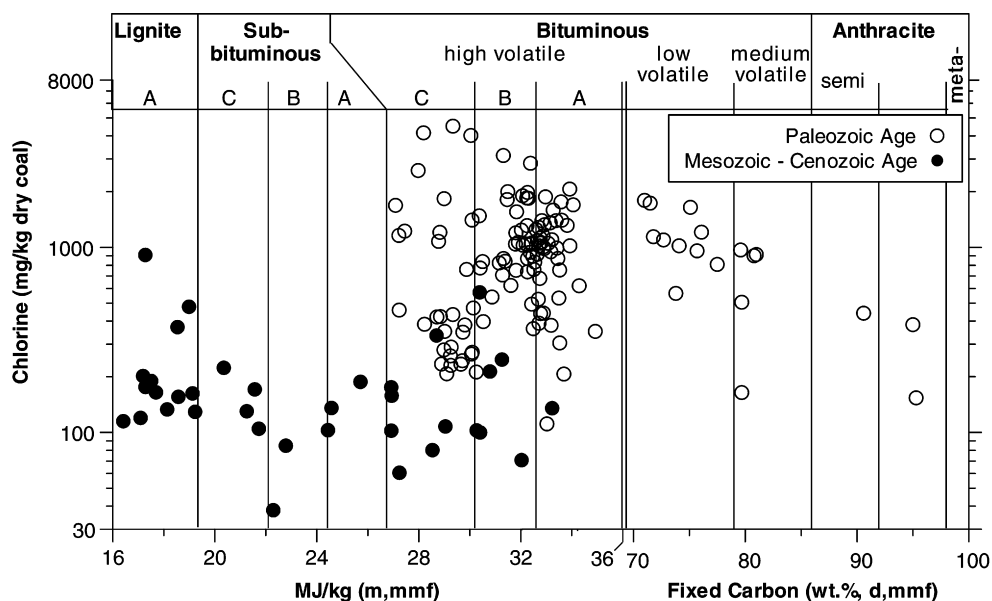


Fig. 8. Chlorine in commercial USA coal complexly varies with ASTM (1990) rank and geologic age. Points show average values for coal produced from USA counties calculated from dry-basis ICR-2 data (USEPA, 2002), estimated moisture (Quick et al., 2005), and county-average fixed C and geologic age from Bragg et al. (1998).

reduce the reactive Cl available to oxidize Hg (Cao et al., 2005). Olson et al. (2003) suggested that S may limit Hg capture by filling Hg binding/reaction sites on fly-ash C. Meij et al. (2002) pointed out that higher flue-gas temperatures required to prevent ductwork corrosion by H_2SO_4 when burn-

ing high-S coal, may also reduce Hg capture, as oxidized Hg in flue gas does not condense above $\sim 140^\circ C$. Regardless of why S reduces Hg capture, this effect complements the likely co-reduction of Hg when coal S is reduced (Toole-O'Neil et al., 1999; Quick et al., 2003). Thus, selection of low-S

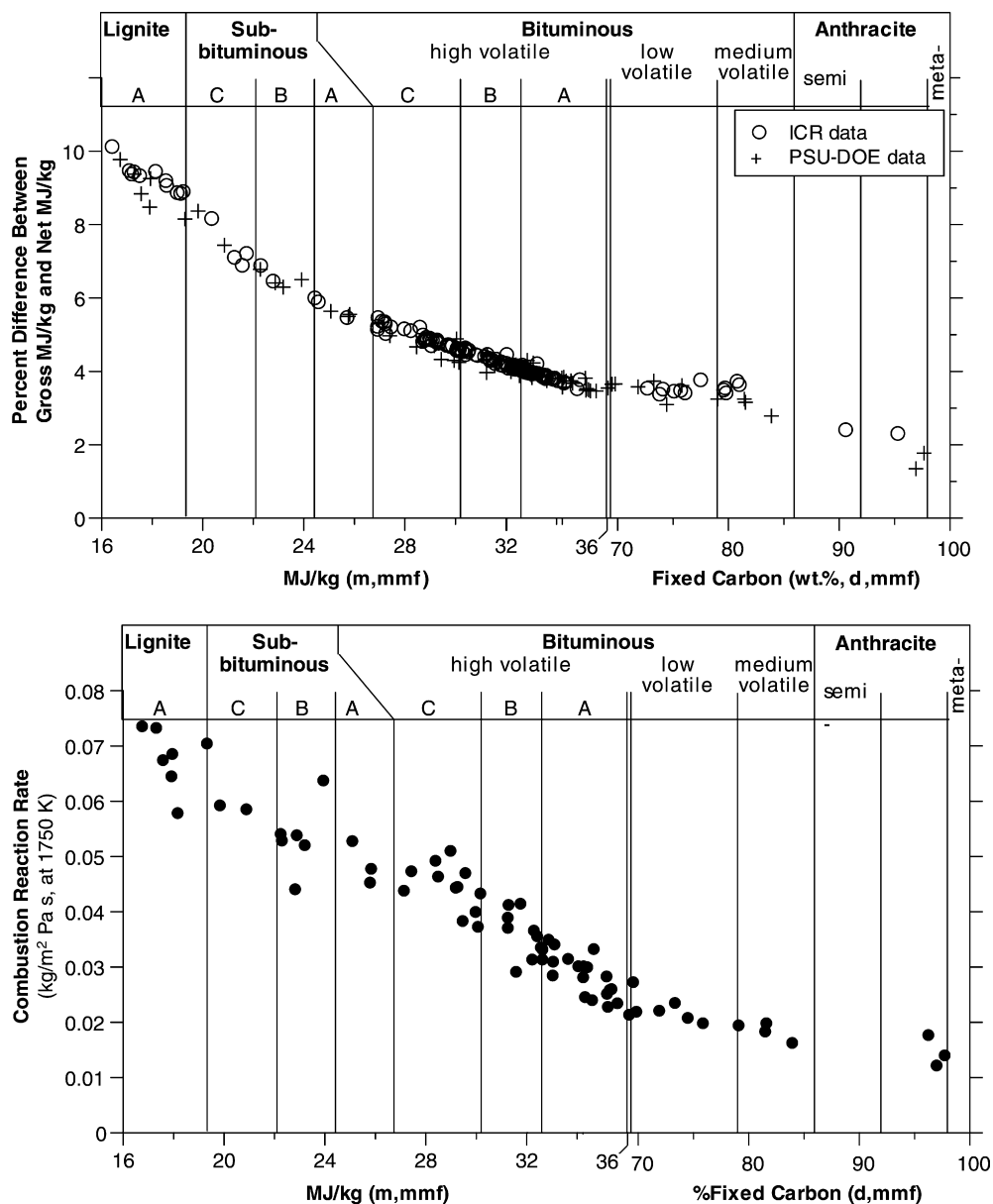


Fig. 9. (top) The difference between the net and gross heating value of USA coal systematically varies with ASTM (1990) coal rank, where: percent difference = $100(MJ/kg_{gross} - MJ/kg_{net})/MJ/kg_{gross}$, and $MJ/kg_{net} = MJ/kg_{gross} - 0.0245(M + 9H)$ where M is wt.% moisture, H is wt.% organic H, and all values are on a moist, whole-coal basis. The PSU-DOE data are single coal assays on an equilibrium moisture basis. The ICR data are county-average values on an estimated, as-shipped moisture basis. Modified from Quick et al. (2005) using assigned fixed C from Bragg et al. (1998). (bottom) Combustion reactivity systematically varies with ASTM (1990) rank; low-rank coal is more reactive than high-rank coal. Coal assay data are from Quick et al. (2005); combustion reaction rate (k) = $\exp[2.8 - 7.58(\text{Carbon}_{(\text{coal,wt.\%})}/(100 - \text{ash}_{(\text{coal,wt.\%})} - \text{moisture}_{(\text{coal,wt.\%})})]$ is from Pallarés et al., 2005).

coal has two likely effects: (1) reducing the Hg content of feed coal, and (2) improving post-combustion Hg capture.

Data from Canadian Electricity Association members (CEA, 2004) also show that coal S reduces Hg capture (Fig. 7). This effect is strongest where both fly-ash C and coal Cl are high, and is consistent with the suggestion that S fills reactive sites on fly-ash C (Olson et al., 2003). This interpretation may also explain why S is not a significant predictor of Hg capture for units equipped with spray dry adsorption, fabric filter technology; in this case, gaseous flue-gas S is converted to a non-reactive solid (sulfate) before it arrives at the particulate filter, where effective Hg capture by fly-ash C presumably occurs.

3.2.4. Coal rank and mercury emissions

The Clean Air Mercury Rule (USEPA, 2005b) established Hg emissions budgets for USA states according to the amount and rank of coal burned in each state. Rank-specific standards for new power plants have also been proposed (USEPA, 2005d). The rule's reliance on rank recognizes that existing emission controls are less effective in controlling Hg emissions from USA plants burning lignite and sub-bituminous coal than those burning bituminous coal (Fig. 4). Coal rank may be useful for regulatory purposes, but it is not a chemical or physical property. However, some coal properties that are closely

related to rank may impact Hg emissions from coal combustion.

Bituminous and higher rank coal typically contains more Cl than lower rank coal (Yudovitch and Ketris, 2006). Chlorine promotes the formation of oxidized, more easily captured Hg species in flue gas (Galbreath and Zygarlicke, 2000), consistent with better Hg capture observed for plants burning bituminous coal (Fig. 4). However, the relationship between Cl and rank of USA coal shows substantial scatter (Fig. 8). Moreover, Mesozoic–Cenozoic bituminous coal in the western USA typically has low Cl concentration. Consequently, the relationship between rank and Cl concentration may be coincidental rather than causative, and more abundant Cl in high-rank coal may obscure any influence of rank on Hg capture.

Although unlikely to inhibit or promote Hg capture by existing emission controls, variation of coal moisture is significant where regulations are specified on an electric output basis, rather than a fuel basis. Specification of emission limits on an electric output basis is more demanding for plants burning high-moisture (low-rank) coal because the coal heating value reported from the laboratory includes the latent heat of water vapor, whereas the coal heating value available to the boiler does not. Unlike the laboratory, combustion in an industrial furnace occurs at constant pressure and the latent heat of water vapor is lost from the furnace with the flue

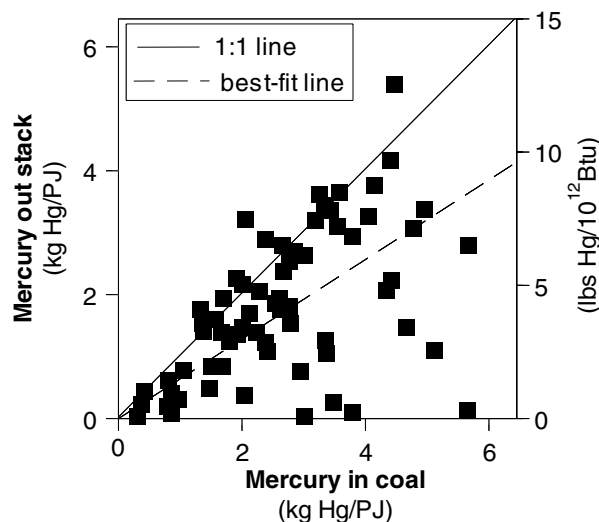


Fig. 10. Mercury emissions vary with the Hg content of coal. The best-fit line corresponds to $Hg_{out} = 0.64 Hg_{in}$, with an $r^2 = 0.27$. Note that many of the units plot near the 1:1 line. Mercury emissions exceeding the Hg content of the coal (units plotting above the 1:1 line) may reflect limited assay precision, limited test duration, and/or difficulty obtaining representative coal samples. Data for 67 conventional, pulverized-coal-fired units are from USEPA (2002).

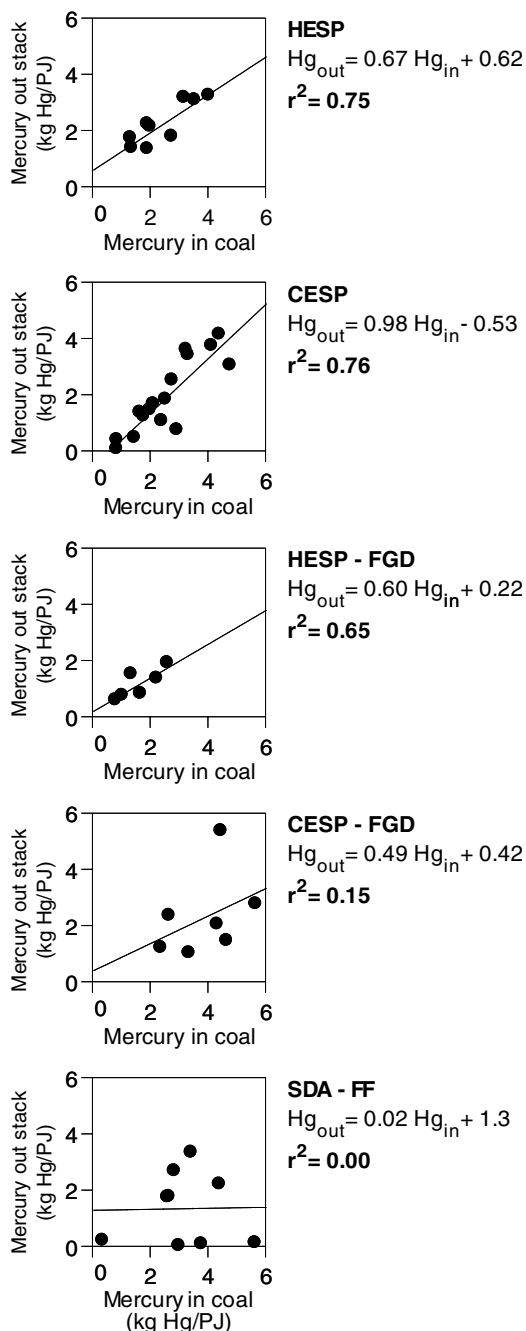


Fig. 11. The significance of coal Hg content depends on the emission control technology. Data from USEPA (2002), where: HESP = hot-side electrostatic precipitator. CESP = cold-side electrostatic precipitator. HESP-FGD = hot-side electrostatic precipitator with wet, flue-gas desulfurization. CESP-FGD = cold-side electrostatic precipitator with wet, flue-gas desulfurization. SDA-FF = spray dry adsorption S control with fabric filter

gas; this heat loss varies with rank (Fig. 9 top). Consequently, burning low-rank (high-moisture) coal reduces boiler efficiency and increases Hg emissions

per MWh electricity produced. Although variation in flue-gas moisture is otherwise unlikely to influence flue-gas Hg capture, it is worth noting that increasing flue-gas moisture may increase Hg capture in systems where UV-irradiated TiO_2 is used to promote Hg oxidation (Rodríguez et al., 2004).

Moisture variation in coal is a consequence of compaction of coal beds during geologic burial (Dulhunty, 1954), resulting in variation in USA coal from nearly 45% by weight (Louisiana lignite) to a minimum near 5% (central Appalachian bituminous). In addition to physical compression, geologic burial also increases temperature, which cleaves labile organic constituents and promotes polymerization of the residual organic matter (Dulhunty, 1954). As coal becomes more aromatic and refractory with increasing rank, larger amounts of unburned C in fly ash are expected. Indeed, Fig. 9 bottom suggests that low-rank coal is inherently more reactive during combustion than high-rank coal. The relationship (Fig. 9 bottom) is consistent with the empirical observation that fly ash from bituminous coal contains more C than fly ash from subbituminous or lignite coal (Sjostrom et al., 2001). Unburned carbon in fly ash is important because it increases Hg capture by existing emission controls (Hower et al., 1999b; Gibb et al., 2000).

Although both theoretical and empirical observations support the idea that increasing rank is responsible for increasing fly-ash C, a causative relation remains unclear. This is because different combustion technology is used for different rank coal. Large furnaces, required to minimize molten ash agglomeration when burning low-rank coal, promote C burnout. Small furnaces, appropriate for bituminous coal with more refractory mineral constituents, provide less time for complete combustion. Combustion modifications to reduce N oxide emissions have increased fly-ash C levels (Hower et al., 1999a), further obscuring any relationship between rank and fly-ash carbon abundance.

3.2.5. Inertinite

Inertinite group macerals include fossil charcoal and other C-rich constituents. As the name implies, inertinites are typically less reactive than other coal macerals and disproportionately contribute to unburned C in fly ash (Sanyal, 1983). Inertinite abundance may be most significant in low-rank coal where chemical differences between the maceral groups are largest (Dormans et al., 1956). Goodarzi (2005) attributed enhanced Hg capture and high fly-

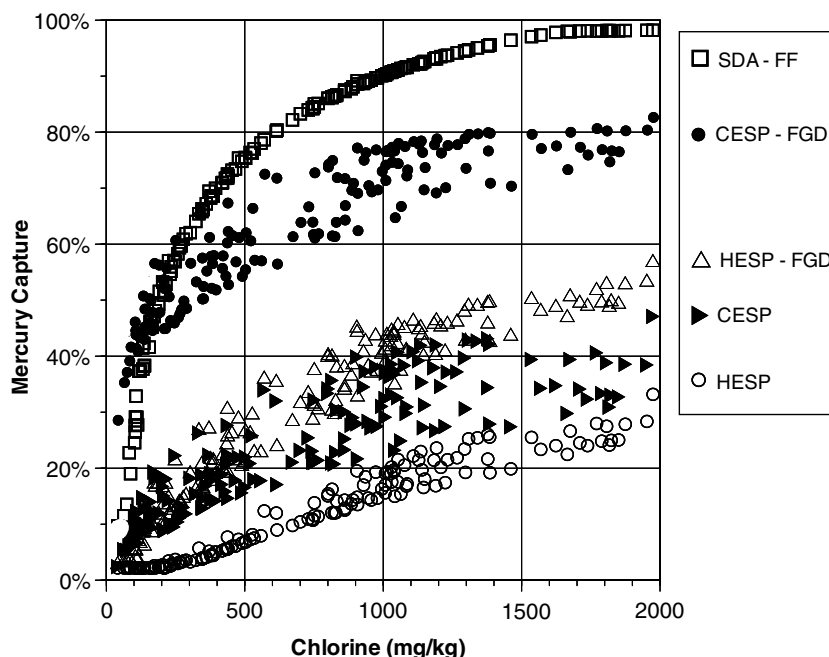


Fig. 12. Predicted Hg capture by APCD's as a function of Cl content in coal. Results are averages of published best-fit equations for each control technology applied to county-average ICR coal assay values (Quick et al., 2005). HESP = hot-side electrostatic precipitator (open circles). CESP = cold-side electrostatic precipitator (solid triangles). HESP-FGD = hot-side electrostatic precipitator with wet, flue-gas desulfurization (open triangles). CESP-FGD = cold-side electrostatic precipitator with wet, flue-gas desulfurization (solid circles). SDA-FF = spray dry adsorption S control with fabric filter (open squares).

ash carbon values to increasing inertinite in Canadian subbituminous feed coal. The effect of inertinite on unburned carbon is less certain for bituminous coal (Borrego et al., 1997). Moreover, optically anisotropic fly-ash carbon from vitrinite group macerals in bituminous coal has a greater affinity for Hg than isotropic carbon derived from inertinite (Hower et al., 2000b).

4. Optimizing co-benefit of existing emission controls

Despite proven emission control technology, burning low-S coal is a popular method to reduce S emissions. Likewise, burning low-Hg coal is a likely method to reduce Hg emissions. Fig. 10 shows that Hg emissions from many USA coal-fired power plants vary systematically according to the Hg content of the coal. The best-fit line indicates that for conventional coal-fired plants, 64% of coal Hg is emitted to the atmosphere and 36% is captured.

The importance of coal Hg concentration depends on the emission control technology (Fig. 11). Note that plants with HESPs or CESPs capture little Hg, and that Hg emissions from these plants can be reasonably estimated from the feed-

coal Hg concentration. In these cases, selection of low-Hg coal should reduce Hg emissions. The Hg concentration of the feed coal is not an accurate predictor of Hg emissions from units with SDAs and FFs, or units with CESPs and wet FGD controls (Fig. 11). In these cases, coal selection or blending, to achieve optimal Cl contents of 500 mg/kg or greater, might be considered (Fig. 12).

Selection of low-S coal should reduce Hg emissions from units equipped with CESPs alone or CESPs and wet FGD (Fig. 7). If the negative effect of S is due to blocking adsorption sites on fly-ash C (Olson et al., 2003), higher C injection rates may be required when activated C is deliberately injected into flue gas to capture Hg, when burning high-S coal.

5. Summary and conclusions

Analysis of results from the ICR and other empirical sources provide estimates of the effectiveness of Hg removal by conventional controls in USA coal-fired utility generating stations. Coal quality, notably Cl and S contents, and the combustion characteristics of the coal both influence Hg

speciation in flue gas entering air pollution control devices. Elemental Hg is difficult to remove from the gas phase, but gaseous oxidized Hg or particulate-bound Hg formed post-combustion can be more readily captured in existing APCDs. For a given coal type, the capture efficiency of these systems varies according to type of device and the conditions of its deployment. Both FF and FGD systems are effective in capturing particulate-bound and oxidized species, respectively, during combustion of bituminous coal. The effectiveness of Hg capture for low-rank coal is lower, due to less efficient oxidation of gaseous elemental Hg. In addition to coal quality and combustion conditions, variables affecting performance for Hg control include the positioning (hot side vs. cold side) of the APCD, and the amount of unburned C in coal ash. Knowledge of coal quality parameters, characteristics of APCDs, and set up of combustion systems allows optimization of Hg capture co-benefit, the primary approach to limiting Hg emissions under the Clean Air Interstate Rule.

Acknowledgements

The authors wish to thank John E. Gray of the US Geological Survey and Mark E. Hines of the University of Massachusetts-Lowell for organizing the mercury session at the 15th V.M. Goldschmidt Conference where an earlier version of this paper was presented. The manuscript was improved with comments from Mark Engle and Hal Gluskoter (USGS), David Tabet and Robert Ressetar (Utah Geological Survey), and Evan Granite (National Energy Technology Laboratory). Portions of this compilation were supported by US Department of Energy contract DE-FG26-03NT41901 to the Utah Geological Survey.

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