



Mercury control technologies for coal combustion and gasification systems

John H. Pavlish*, Lucinda L. Hamre, Ye Zhuang

University of North Dakota Energy, Environmental Research Center, 15 North 23rd Street, Stop 9018, Grand Forks, North Dakota 58202-9018, USA

ARTICLE INFO

Article history:

Received 15 September 2008

Received in revised form 22 April 2009

Accepted 26 May 2009

Available online 12 June 2009

Keywords:

Mercury control

Coal combustion

Advanced power systems

Gasification

Multipollutant control

ABSTRACT

Development and testing of mercury control technologies have largely focused on coal-fired combustion systems, with less emphasis on advanced power systems. Mercury control is influenced by coal properties and chemistry, plant configuration, pollution control devices, flue gas conditions, and plant operations, which differ between combustion and gasification systems. Sorbents such as treated activated carbons have shown promising results in low-temperature environments; however, elevated temperature and reducing environments of many advanced systems remain challenging, requiring research and development to obtain acceptable mercury control levels. Concurrent pollutant/multipollutant control strategies that include CO₂ control are critically needed for both conventional and advanced power systems.

© 2009 Elsevier Ltd. All rights reserved.

1. Background

Technological advances for mercury control have primarily resulted in response to pending regulations put forth in the United States through the US Environmental Protection Agency (EPA) Clean Air Mercury Rule (CAMR), which has now been vacated, and the Clean Air Interstate Rule (CAIR), which was overturned but reinstated in modified form, and in Canada through the Canada-Wide Standards (CWS), and in Europe through more strict control of SO₂ and NO_x. Most mercury control technologies have been developed for and tested on conventional pulverized coal (pc)-fired power plants, with limited, yet growing development of technologies applicable to advanced power systems such as ultrasupercritical and fluid-bed combustion, oxycombustion, and gasification systems. Several key factors affect mercury emission and subsequent capture, including coal chemistry, plant configuration, pollution control devices, unit temperatures and pressures, and operational conditions. Several technologies are considered mature, especially those used for concurrent control of SO_x, NO_x, and particulate matter (PM)—these demonstrate some mercury capture as well. Sorbent technologies, especially activated carbons, have proven to be a reliable, relatively low-cost mercury control option in low-temperature environments and show some ability to capture mercury in advanced power systems, although elevated temperature and reducing environments have proven to be challenging and need significantly more research to arrive at acceptable mercury control strategies. Concurrent multipollutant control, both

in conventional and advanced power systems, is desirable, especially if CO₂ control can be easily integrated.

2. Regulatory drivers

Worldwide, mercury reductions are being sought either by regulations that are specific and targeted at mercury emissions from coal-fired power plants or are being achieved by regulations that seek more strict multipollutant control of SO₂, NO_x, and PM. For example, in the United States, EPA announced in 2000 the need to regulate mercury emissions from coal-fired electric generating units under the 1970 Clean Air Act (CAA). At that time, a dedicated effort was already under way in both the United States and Canada to better understand the fate and formation of mercury, including native capture in existing coal-fired power plants, most of which are pc-fired units. The world's first mercury control regulation was released by EPA on March 18, 2005—the CAMR [1]. A sister rule promulgated just prior to CAMR, the CAIR, was crafted concurrently to provide early multipollutant control for mercury by controlling SO_x, NO_x, and PM [2]. Despite earlier expectations that EPA would release a rule that called for maximum achievable control technology (MACT) standards, CAMR called for a cap-and-trade approach. After significant input from both the private and public sector, a lawsuit was brought against EPA. The recent outcome of that suit is that the District Court of Appeals vacated CAMR on February 8, 2008, leaving EPA with instruction to draft a new regulation, which means that utilities in the United States will soon be required to comply with MACT standards.

Since the 1990s, Canadians have also been evaluating mercury control options for their power plants and gathering data from

* Corresponding author. Tel.: +1 701 7775268; fax: +1 701 777 5181.
E-mail address: jpavlish@undeerc.org (J.H. Pavlish).

Nomenclature

CAA	Clean Air Act	IGCC	integrated gasification combined-cycle
CAIR	Clean Air Interstate Rule	LOI	loss on ignition
CAMR	Clean Air Mercury Rule	MACT	maximum achievable control technology
DOE	US Department of Energy	MSW	municipal solid waste
EERC	Energy & Environmental Research Center	NETL	National Energy Technology Laboratory
EPA	US Environmental Protection Agency	NODA	Notice of Data Availability
ESP	electrostatic precipitator	pc	pulverized coal
FACT	Facility for the Analysis of Chemical Thermodynamics	PE	purchased equipment
FBC	fluidized-bed combustion	PM	particulate matter
FF	fabric filter	TCC	total capital costs
GHG	greenhouse gas	TDF	tire-derived fuel
GTI	Gas Technology Institute	WRI	Western Research Institute
ICR	Information Collection Request		

existing units, especially through the efforts of the Canadian Electricity Administration. In 2006, the CWS was released, which set a federal mercury cap requiring a 70% overall reduction in mercury from coal-fired power plants.

Japan, China, Australia, Mexico, Russia, and the European countries are evaluating and estimating mercury emissions from their coal-fired sources but to date have not issued regulations targeted directly at mercury reductions. However, many of these countries are pursuing/achieving mercury emissions reductions through implementation of improved control of SO₂, NO_x, and PM.

3. Factors affecting mercury emission from coal-fired combustion

Coal-fired power plants comprise the largest source of anthropogenic mercury emissions in the world [3] and are the largest anthropogenic source of mercury emitters in the United States [4,5]. In 2005, a study indicated that coal represented slightly over half of the fuel for the United States and about 19% of the fuel for Canada [6], although this number may fall given Ontario's insistence that it will retire its coal-fired fleet. Coal-fired utilities are also the largest source of mercury emission in Canada; of the 9 tonnes of mercury emitted, Environment Canada has determined the majority comes from coal-fired generation [7]. A 2008 report from the United Nations Environmental Programme (UNEP) compiling 2005 data showed North American (the United States and Canada) mercury emissions from coal-fired utilities to be approximately 153 tonnes a year; emissions from electricity producers in this region currently are about 7.9% of global mercury anthropogenic emissions but have decreased over the last decade [8]. The same report indicates that global, anthropogenic mercury emissions in 2005 were about 1930 tonnes, of which 45.6% was from power and heat stationary combustion sources [8].

Unlike NO_x or SO_x emissions, which have been reduced successfully for well over a decade, controlling mercury emission is far more complicated. As a trace metal, mercury concentrations are significantly lower than other emissions controlled to date and can be quite variable, depending upon the coal type and chemistry. Low concentrations in the flue gas affect mass-transfer reactions, limiting kinetic reactions in systems that typically have short residence times. In addition, flue gas chemistry is likely to impact mercury, changing its speciation and, thus, its reactivity and potential for capture. The halogen concentration (e.g., chlorine) present in the flue gas is especially important; higher halogen concentrations result in higher ratios of mercury oxidation than low-halogen coal [9].

In addition to coal/flue gas constituent chemistry, particulars of the generation system will also affect the amount of mercury emitted.

Just as each coal is unique and will result in slightly different flue gas constituents compared to others in its respective rank, each coal-fueled unit will also result in different mercury speciation and emissions as a result of system type, configuration, and operation of the unit (temperature, pressure, and other operational parameters such as level of unburned carbon). Elemental mercury is generally not captured and emitted, whereas oxidized mercury tends to be soluble in water and frequently becomes particulate-bound, aiding in its capture by pollutant control devices such as those currently used for SO_x, NO_x, and PM. For example, US EPA officials have estimated that use of these control devices, among other strategies, has already resulted in a reduction of mercury emissions; US mercury emissions from 1990 to 2002 have already fallen by about half, with further reductions expected as a result of other mercury control regulations [10].

4. Mercury control technologies for conventional coal-fired power plants

Much of what has been learned regarding mercury chemistry, speciation, and capture comes from studies of traditional coal combustion power plants. Furthermore, to understand technology options for advanced power systems, it is helpful to understand the technology choices that are available/applicable to traditional coal combustion plants. As can be seen from Table 1, mercury reductions from coal combustion plants can range from 0% to 90% and are highly dependent on coal type and how the plant is equipped with existing SO₂, NO_x, and particulate control devices for multi-pollutant control. Beyond these conventional technologies, there are other technologies, as shown in Table 2, that have been developed, tested, and are now being commercialized that show promise for reducing mercury emissions from conventional coal combustion sources. As summarized in Table 2, these technologies include fuel blending, sorbent technologies, and scrubbing technologies as well as boiler treatment additives, coal pretreatment/cleaning strategies, coal and sorbent additives that induce oxidation and better mercury capture, and regenerable sorbents. A number of emerging technologies are also being investigated that are generally not commercially available or have limited test data, as summarized in Table 2. It should be recognized, however, that there are few technologies that can be applied universally at all coal-fueled electric generating facilities because of differing plant configurations and coal types. To evaluate a technology's applicability and potential effectiveness, technical details of the technology must be evaluated that include its advantages and its limits/constraints and how these are affected by unique plant considerations, coal type, boiler type, and trace metal emissions, with careful thought regarding possible negative impacts to the overall

Table 1

Expected mercury removal from existing pollution control devices at US power plants.

Control technologies	Typical mercury removal based on aggregate data (%) ^a			
	Bituminous	Subbituminous	Lignite	All coals
Cold-side ESP	30–40	0–20	0–10	0–40
Cold-side ESP + wet FGD ^b	60–80	15–35	0–40	0–80
Dry FGD + cold-side ESP	35–50	10–35	0–10	0–50
Fabric filter	40–90	20–75	0–10	0–90
Fabric filter + wet FGD	75–95	30–75	10–40	10–95
Dry FGD + fabric filter	65–95	20–40	0–20	0–95
Coal cleaning	20–40	?	?	0–40

^a Typical values based on EPA Notice of Data Availability (NODA), ICR data, field tests, and observations. Some values are based on single data points and may not reflect removal for all plants.

^b Flue gas desulfurization.

Table 2

Commercial maturity of mercury control technologies for coal combustion.

Commercially promising technologies	Commercially emerging technologies	Developing technologies
<ul style="list-style-type: none"> • Energy efficiency and conservation <ul style="list-style-type: none"> – Improved plant generation efficiency – Improved-efficiency consumer products – Energy use conservation • Demand-side management <ul style="list-style-type: none"> – Peak power management programs – Green power programs • Fuel blending <ul style="list-style-type: none"> – Natural gas – Oil – Biomass – Petroleum coke – Coal blending – Tire-derived fuel • Fuel switching <ul style="list-style-type: none"> – Switching to a mercury-compliant coal – Repowering with natural gas – Repowering with residual or distillate oil – Switching to biomass • Fuel cleaning or pretreatment <ul style="list-style-type: none"> – Conventional • Noncombustion sources <ul style="list-style-type: none"> – Nuclear and hydroelectric – Wind and solar • Activated carbon injection • Conventional scrubber technology 	<ul style="list-style-type: none"> • Advanced coal cleaning/pretreatment <ul style="list-style-type: none"> – K-fuel process – GRE fluid-bed drying process – Western Research Institute (WRI) drying process – EERC hydrothermal techniques • Combustion modifications <ul style="list-style-type: none"> – GE EER – process and system to reduce mercury emission by combustion modification – Lehigh University – increased loss on ignition (LOI)/temperature modifications – US Department of Energy (DOE) National Energy Technology Laboratory (NETL) – thief process for the removal of mercury from flue gas • Treated activated carbons <ul style="list-style-type: none"> – Sulfur-impregnated carbons – Halogenated carbons • Iodine-impregnated carbons • Brominated carbons • Chlorinated carbons • ALSTOM – Mer-Cure™ • Sorbent enhancement additives • Noncarbon sorbents <ul style="list-style-type: none"> – Sodium tetrasulfide (Na₂S₄) – Amended silicates – Calcium-based sorbents • Fixed sorbent (carbon) beds • Electric Power Research Institute MerCAP™ • Mercury oxidation technologies for wet FGD applications • Oxidation/scrubber technologies • PowerSpan – electrocatalytic oxidation (ECO™) 	<ul style="list-style-type: none"> • Advanced cleaning/separation <ul style="list-style-type: none"> – Magnetic separation – Advanced froth flotation – Selective agglomeration – Chemical methods – Biological methods • Novel sorbents <ul style="list-style-type: none"> – Metal oxide-based sorbents • Noncarbon fixed beds • Mercury control with the advanced hybrid particulate collector felt filter bag inserts • Pahlman Process (EnviroScrub) • Airborne process – sodium bicarbonate scrubbing • Advanced dry scrubbing • LoTox™ – combined oxidation of NO_x and mercury • DOE NETL – photochemical oxidation (PCO™) • McDermott Technology Inc. – condensing heat exchanger

system, such as an unintended increase in other emissions. Effectiveness must also take into consideration the impacts on by-products, such as fly ash, that can often have a significant economic value [11].

As mentioned earlier, the present business climate at electric generating facilities is already infused with a tremendous amount of risk. No technology, no matter its applicability and effectiveness, will be implemented if the economics, including both operating and capital costs, are not weighed. Some technologies are capital-intensive (e.g., scrubbers), while others have a low-capital cost, but have relatively high operating costs (e.g., sorbent injection). Depending upon a unit's expected production life, some technologies that involve high capital investments may be warranted. If a unit is nearing retirement, low-capital strategies are most likely

to be implemented. Often, the ongoing expenditures in personnel, balance-of-plant effects, and replacements can exceed initial investments in hardware and consumables.

Related to the economics is an evaluation of commercial maturity (as shown in Table 2) which is a good indication of whether performance guarantees will be available and the level of risk that the utility must bear. Generally, existing emission controls that are already used for other pollutants and that provide concurrent pollutant control are favored above those that have limited data on performance and reliability. This is especially true in a facility that has a very tight footprint—thus little flexibility to install new technologies on top of existing retrofits. All of these factors must be considered when the most appropriate and cost-effective technology to implement at a given plant is chosen.

5. Mercury control technologies for advanced coal-fueled power plants

As the North American power plant fleet ages, replacement with more advanced power systems is being considered. Generally speaking, advanced power systems provide the opportunity to address environmental issues and to operate generally at higher temperatures, increasing overall efficiency and, thereby, reducing emissions considerably. However, these plants are more complex and far less common than the traditional coal-fired systems used most commonly throughout the world. It is unlikely, however, that this trend will continue as worldwide concerns over CO₂ emissions will drive utilities to install more advanced systems such as the following:

- Supercritical (1000° to 1100 °F [538° to 593 °C], >3200 psia [22 MPa]) and ultrasupercritical (1100° to 1300 °F, >3500 psia [24 MPa]) plants.
- Fluidized-bed combustion (FBC) plants.
- Oxycombustion plants.
- Integrated gasification combined-cycle (IGCC) plants.

While initially there appeared to be a clear advantage to using IGCC when CO₂ reductions were considered, most recent performance and economic data suggest that all options are competitive when technology advantages/disadvantages and plant-specific considerations are taken into account (www.netl.doe.gov/energy-analyses/baseline_studies.html). In terms of mercury reductions, each of the advanced power systems is quite different from conventional power systems and has unique design and operating characteristics that can either facilitate mercury capture or make capture more challenging. These aspects are discussed in more detail as follows.

5.1. Fluidized-bed combustion systems

FBC systems are unique in that they are typically very flexible-fuel systems, providing the opportunity to combust coal with biomass, tire-derived fuel, municipal solid wastes, etc. Most of the world's FBC systems are in Europe, but they are becoming more attractive to North American power producers, especially for distributed energy. These systems tend to be much smaller than pc-fired systems and generally operate at lower temperatures, thereby generating less NO_x.

In FBC systems, limestone is typically used as a bed material along with coal or, typically, a coal-biomass blend. Consequently, mercury can come from both the bed material (limestone) and the fuel. This can contribute to significant variability as both streams individually can be highly variable in mercury concentration. In an FBC system, several feedback/recycle loops reuse the limestone and fly ash to maximize use of bed material. These recycled materials, along with new bed material, are fed continuously to keep the bed at a proper depth. The overall bed composition is <5% of fuel by weight. The fuel is constantly surrounded by hot,

moving limestone bed material. Because there is such good heat transfer between the fuel and bed material, combustion temperatures in an atmospheric circulating fluidized-bed (CFB) unit are lower than in conventional systems—about 1470° to 1650 °F (800° to 900 °C) compared to boiler temperatures of 1900° to 2200 °F (1038° to 1204 °C) for conventional pc-fired boilers. As a result, the limestone captures sulfur emissions very effectively at these temperatures, and the systems have inherently lower NO_x emissions than conventional coal-fired systems.

Because of this system of recycle loops, it is very difficult to conduct a proper mercury mass balance. Fewer than ten of the 84 plants selected for EPA's ICR Phase III emission testing were equipped with FBC systems, resulting in very limited mercury emission data for these systems. Because this subcategory represents a range of fuels, fluid-bed types, and particulate control devices, the full-scale data are not sufficient to evaluate the mercury emissions from these units thoroughly. Given the available data, removal efficiencies ranged from 44% to 99% with a variety of fuel types; the majority were equipped with a fabric filter (FF) (see Table 3) [12].

The Energy & Environmental Research Center (EERC) conducted a project to evaluate mercury emissions and control options for three coals—a North Dakota lignite, a Texas lignite, and a Wyoming subbituminous coal—in a pilot-scale CFB combustor utilizing limestone as bed material and equipped with a FF and spray dry adsorber [13]. Mercury control options were evaluated including injection of standard activated carbon and a proprietary fuel additive designed to promote Hg⁰ oxidation and capture, as shown in Table 4. For baseline tests with all coals, the majority of the mercury was in the elemental form (Hg⁰), which is the hardest to capture. As Table 4 shows, the furnace additive alone promotes capture, but the greatest control is shown when an additive to promote mercury oxidation is coupled with activated carbon, approaching and sometimes exceeding 90% mercury capture at fairly low levels of injection and additive addition. However, during the tests with the Wyoming coal, given the low FF inlet Hg concentration during the activated carbon injection tests, residual furnace additive was probably present from previous testing and positively biased the Hg removal results. During all tests, >90% Hg capture was obtained through one or more forms of Hg control strategies, although the best strategy depended on the coal and emission control device configuration [13].

5.2. Oxycombustion

Oxycombustion is a relatively new concept that is primarily driven by CO₂ concerns. While conceptually the use of relatively pure oxygen for combustion will result in nearly pure streams of CO₂, many practical issues still need to be resolved and/or understood. For example, the use of pure oxygen will alter flame temperatures and will reduce flue gas flow rates, significantly changing the heat transfer within the radiative and convective zones of the boiler. CO₂ may be recycled to compensate and increase mass flow rates to improve heat transfer characteristics; however, the flue gas chemistry will be vastly different from conventional coal combus-

Table 3
Mercury removals noted in EPA ICR data.

Plant name	Fuel type	Emission control device	Total Hg, inlet (lb/TBtu)	Total Hg, stack (lb/TBtu)	Removal (%)
Heskett Station, B2	Fort Union lignite	Multicyclone/ESP	3.32	1.73	48
TNP-One Station, Unit 2	Lignite	Fabric filter	25.88	10.87	58
Scrubgrass Generation Station, Unit 1	Waste bituminous	Fabric filter	92.8	0.147	99
AES Hawaii, Unit B	Indonesian bituminous	Fabric filter	1.28	0.6	54
Kline Township Generating Plant, Unit 1	Anthracite-bituminous	Fabric filter	52.06	0.521	99
Stockton CoGen Plant	Petroleum coke-bituminous	Fabric filter	1.96	0.02	99

Table 4

EERC tests in a CFB unit to evaluate mercury control by standard activated carbon with and without proprietary furnace additive.

	Rate (lb/Macf)	Hg removal (%)	
Injection test		FF	SDA-FF
North Dakota lignite, 7.8 μg/dNm ³ mercury concentration (>90% Hg ⁰)			
Baseline	–	26	26
Furnace additive 2	1.9	86	68
Standard activated carbon	1.0	71	82
Standard activated carbon	1.8	92	95
Standard activated carbon	2.5	89	90
Texas lignite, 22.7 μg/dNm ³ mercury concentration (>70% Hg ⁰)			
Baseline	–	80	50
Furnace additive 2	0.45	94	62
Furnace additive 2	1.1	96	86
Standard activated carbon	0.45	85	69
Standard activated carbon	0.89	85	79
Standard activated carbon + furnace additive 2	0.45/0.89	93	91
Wyoming subbituminous, 12.1 μg/dNm ³ mercury concentration (>90% Hg ⁰)			
Baseline	–	27	NA
Furnace additive 2	0.51	61	NA
Furnace additive 2	1.0	72	NA
Furnace additive 2	2.0	84	NA
Furnace additive 2	3.0	87	NA
Standard activated carbon	0.39	74	NA
Standard activated carbon	0.79	80	NA
Standard activated carbon	1.60	89	NA
Standard activated carbon + furnace additive 2	0.79/0.51	83	NA

NOTE: Removals based on measured Hg in flue gas with CMMs (using inlet CMM data for the ND and TX lignite runs and inlet OH data for the WY run).

tion flue gases, from which most current data and experience are derived. As a result, mercury transformation mechanisms in post-oxygen-coal combustion flue gas will not be the same and are not well understood at present. So far, only preliminary equilibrium calculations using FACT (Facility for the Analysis of Chemical Thermodynamics) have been performed to understand partitioning and emissions of Hg, Se, As, and Cd in O₂/CO₂-rich gases [14].

Studies on char combustion have shown that elevated CO₂ concentrations surrounding the burning char particles will not significantly affect the kinetics of char oxidation with O₂ because of the lower reaction rates of char–CO₂ than that of char–O₂ [15,16]. On the other hand, elevated O₂ concentrations plus higher char combustion temperature cause significant CO oxidation in the boundary layer [17]. The high char combustion in an elevated O₂ environment may change the vaporization rate of trace metals, including mercury. To date, limited to no experimental data are available on mercury vaporization and transformation during oxygen–coal combustion.

Another unknown concern is NO_x, which appears to be less than one-third of that in conventional air–coal combustion, largely as a result of the reduced volume of flue gas [18]. This NO_x reduction is thought to be the result of several potential mechanisms: (1) decreased thermal NO_x due to a low concentration of N₂ from air (now oxygen) in the combustor; (2) the reduction of recycled NO_x in the volatile matter release section; and (3) the interactions between recycled NO_x (when recycling CO₂), fuel N, and hydrocarbon released from coal [19]. The recycle loop back to the combustion zone may actually increase the concentration of NO_x in oxyfuel combustion flue gas, which is also likely to affect mercury oxidation, since NO is recognized as playing an important role in mercury oxidation in coal flue gas in conventional combustion. Preliminary experimental data indicate NO has a minor effect on Hg oxidation in an O₂/CO₂ simulated flue gas environment [20].

In an oxyfuel combustion scenario, SO₂ concentrations in the flue gas are higher than from conventional air–coal combustion, primarily due to flue gas (CO₂) recirculation. Higher SO₂ concentration also results in higher SO₃ and possible sulfur retention by ash

[21], which may impose significant challenges for mercury control in oxyfuel combustion flue gas since SO_x (SO₂ and SO₃) compete with mercury for adsorption sites on the sorbent surface. In addition, moisture level in oxyfuel combustion flue gas will increase as a result of flue gas recycling, also affecting mercury sorbent performance.

In summary, although data are limited, it is clear that oxyfuel combustion dramatically changes the flue gas chemistry; therefore, mercury partitioning and transformation mechanisms will be altered. Thus significant research is still needed in this area.

5.3. Gasification systems

Gasification technologies, in particular IGCC, offer many advantages over conventional power systems, as follows:

- IGCC technology provides for low SO₂, NO_x, and CO emissions.
- CO₂ can be captured more efficiently with IGCC than with conventional technologies. The CO₂ could be sequestered or sold in part as a by-product, possibly producing a revenue stream.
- Overall efficiency for IGCC is approximately 40–45% compared to conventional coal plants at approximately 30–35% efficiency. However, technological advancements have been made to ultrasupercritical units, which now are expected to exceed 45%.
- Water requirements are typically about 50% less for IGCC applications than for conventional coal generation.
- Marketable by-products from the IGCC process can be sold, such as sulfur.

While there are advantages to IGCC, there are also some disadvantages:

- IGCC facilities are more expensive to build than conventional coal plants, and because of limited installations, experience is limited, which could result in inaccurate cost estimates.
- Reliability is not as good, and maintenance for IGCC is more frequent and of longer duration, resulting in a need for additional purchased power.

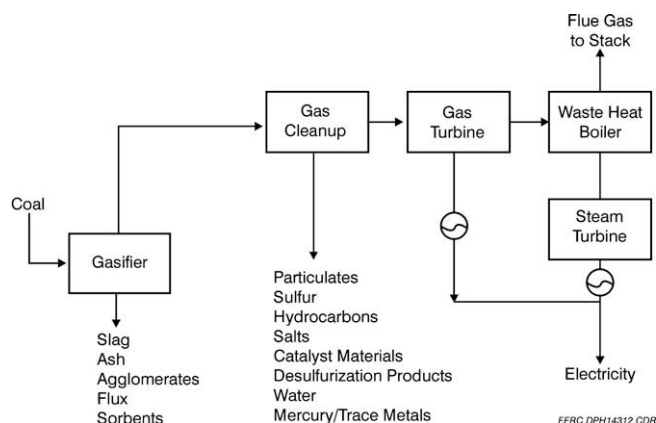


Fig. 1. Schematic of the IGCC process, including wastes and by-products.

- Limited experience with various coal types, in particular low-rank coals [22].
- Performance guarantees are generally not offered or add significant cost if they are.

Although IGCC systems have long been considered a viable clean coal technology that reduces significant emissions, including greenhouse gases (GHGs), very few have been built and operated commercially. Although considered a mature technology, the initial capital expense has proven to be prohibitive, unless CO₂ capture is included in the analysis [22] (see www.netl.doe.gov/energy-analyses/baseline_studies.html). With the potential of regulation to lower GHG emissions and large-scale projects under way to evaluate capture and sequestration of CO₂, there is a renewed level of interest in IGCC systems.

In an IGCC plant, a coal gasification unit is coupled with a gas-fired turbine, replacing the conventional coal-fired boiler. Fig. 1 shows a simple schematic of the IGCC process. At present, four commercial IGCC systems are operating in the world—two in the United States and two in Europe, as summarized in Table 5. Several US planned units have been canceled recently.

In the United States, the Polk Plant, located about 40 miles from Tampa, Florida, produces 250 MWe and is operated by Tampa Electric. Although the plant was originally feeding a high-sulfur bituminous coal, it has been shown to be also capable of using petroleum coke, which it has been using more recently. The facility was built as a US Department of Energy (DOE) demonstration and has been operating since September 1996.

The other IGCC plant in the United States is the Wabash River Plant, which is operated by Global Energy, Inc. It is located near Terre Haute, Indiana, and produces 262 MWe. A smaller unit was constructed as a demonstration site for DOE and has been operated since August 1995. The full-scale facility, operated since 1997, uses gasification technology developed by ConocoPhillips (formerly E-GAS). This facility uses a bituminous coal–water slurry, but is bottom-fed versus top-fed.

While other systems have previously been constructed and operated for short periods, assisting in the development of IGCC, they are not operational at this time in the United States. Of interest, in 2007, an IGCC plant was to be built in Florida, but the permit was rejected because the application did not address CO₂ adequately.

Although IGCC plants were not designed with the goal of mercury removal, the plants still show fairly good native removal rates—the EPA ICR data showed ~60% of the mercury was emitted at the stack, mostly in the elemental form [25]. Table 6 shows the mercury speciation in flue gas from the two noted IGCC plants [26].

Although some mercury is removed, using IGCC as presently configured does not provide adequate removal sufficient to meet anticipated future regulations. Further, it should be noted that a significant amount of the mercury emitted at the stack is elemental, which largely escapes conventional emission control devices.

As can be seen from Table 6, mercury mass balances are difficult to perform for IGCC power plants, with uncertainties in measurement state of art that currently are considered valid for coal-fired generation. Although error bars are not available for this table, experience at the EERC and other organizations studying trace metals in IGCC environments has shown that mercury measurement is extremely difficult and uncertain at present. To further complicate the issue, the complexity of the system allows for potential removal of mercury at numerous steps. Although native capture would seem inadequate, mercury capture can be obtained with IGCC systems at potentially some of the lowest costs of any coal-fired system once it is operational, although the initial costs of building the system continue to increase significantly beyond earlier estimates. Because of the high pressure inherent in IGCC systems, many of the problems associated with the use of sorbents is less of a problem than in conventional systems. Also, because a relatively small volume of gas is treated relative to the flue gas stream in a conventional coal-fired boiler system, the capacity of the sorbent is maximized.

In terms of determining what mercury control options are most effective, one must first understand the temperature to which the gas will be cooled before it is cleaned prior to going into the turbine (see Fig. 1). Generally speaking, gas cleanup can be thought to occur at hot temperatures (above 1000 °F [540 °C]), at warm-gas temperatures ranging from 300° to 1000 °F (150° to 540 °C), or at cold-gas temperatures below 300 °F (150 °C), or typically around 100 °F (40 °C). Since hot-gas cleanup continues to present many challenges, DOE has more recently focused efforts on warm-gas cleanup, with temperatures ranging from 300° to 700 °F (150° to 370 °C). Recent preliminary data suggest that mercury capture tends to be the limiting factor as gas temperatures approach 700 °F (370 °C), although arsenic and selenium are also potential issues because of volatility at fairly low-temperatures (down to 650 °F [340 °C]). Consequently, the focus has now shifted toward warm-gas cleanup at temperatures preferentially ranging from 400° to 500 °F (200° to 260 °C). This is also the temperature range at which phase-shift catalysts can be utilized, such as Fischer–Tropsch, thereby providing the opportunity to generate streams of hydrogen and other useful by-products.

ACs have been used at municipal waste-to-energy facilities for a number of years to remove relatively high levels of mercury very effectively. ACs have also been shown to be somewhat effective on both conventional and IGCC systems, with work being done by the EERC and many others. For example, sulfur-impregnated sorbents were used successfully by the Gas Technology Institute (GTI) and Siemens Westinghouse to remove contaminants from the gas stream of a two-stage IGCC system [27]. A study conducted by Parsons Infrastructure and Technology Group, with technical input from the Eastman Chemical Company, developed detailed cost estimates involving the use of fixed, packed beds of sulfur-impregnated AC [24]. The Parsons–GTI group found that the sulfur-impregnated carbon had a relatively long life and could sustain mercury capture as high as 20 wt% of the carbon. The project examined the use of these sorbents with various feedstocks, including anthracite, bituminous, and subbituminous coal; lignite; tire-derived fuel (TDF); and waste bituminous and anthracite coals. Even in a bituminous coal with 1300 ppbw mercury, the mercury loading of the sorbent after 18 months of use was still only 9.6 wt%. The study noted that Eastman Chemical uses the sulfur-impregnated carbons in its beds to achieve 90–95% mercury removal. Further, the study documented that using two beds in

Table 5

Summary of commercial IGCC projects in operation in the United States and Europe.

Name and plant information	Fuel ^a	Name/type of gasifier	Size (MWe)	Years of operation	Reaction temperature (°F/°C)	Cleanup temperature (°F/°C)	Hg removal
Eastman Chemical Plant Kingsport, TN	C	Chevron-Texaco Entrained Flow (water slurry)	–	1983 to present	?	86° to 100 °F (30 °C) 900 psi	90–95% (Calgon's HGR-P) ^c –
Cool Water (Texaco) Daggett, CA	C	Chevron-Texaco Entrained Flow (water slurry)	125	1984 to 1988			
LGTI Project (Dow/Destec) Plaquemine, LA	Bit. Sub.	Global Energy E-GAS Entrained Flow (water slurry)	160	1987 to 1995			69.6% ^b
Wabash Plant (PSI Energy) West Terre Haute, IN	C	Global Energy E-GAS (Destec) Entrained Flow (water slurry)	262	1995 to present	2300° to 2600 °F (1260° to 1430 °C)	1260° to 1450 °F (680° to 790 °C)	32.3% ^b
Polk Plant (Tampa Electric) Polk County, FL	C	Chevron-Texaco Entrained Flow (water slurry)	250	1996 to present	2500° to 2700 °F (1370° to 1480 °C)	1260° to 1450 °F (680° to 790 °C)	41.6% ^b
NUON Plant (Demkolec) Buggenum, Netherlands	C	Shell Entrained Flow (dry, N ₂ carrier)	253	1994 to present	~2000 °F (~1000 °C)		
ELCOGAS (Puertollano, Spain)	Bit. C/ Pet.	Prenflow/Uhde Entrained Flow (dry)	298	1998 to present	~2300 °F (~1260 °C)		

^a C = coal; Bit. = bituminous; Sub. = subbituminous; Pet = petcoke.^b Ratafia-Brown et al. [26].^c Rutkowski et al. [27].**Table 6**

Mercury removal of Polk and Wabash power plants [6].

Flue gas mercury emissions ^a	µg/Nm ^{3b}	lb/h	% of total
<i>Polk power plant, 250 MWe</i>			
Coal mercury (mercury in)		<0.0207	
Mercury emissions		0.01210	
Particulate-bound mercury	<0.01	0.00003	0.25
Oxidized mercury	0.29	0.00087	7.08
Elemental mercury	3.81	0.01120	92.67
Difference between inlet and outlet mercury ^c = 58.45%		0.00860	
<i>Wabash power plant, 262 MWe</i>			
Coal mercury (mercury in)		0.016	
Mercury emissions		0.01079	
Particulate-bound mercury	<0.02	0.00006	0.56
Oxidized mercury	<0.9	0.00273	25.30
Elemental mercury	2.64	0.00800	74.14
Difference between inlet and outlet mercury ^c = 67.00%		0.00521	

^a Average values for three tests.^b Nm³ = 0 °C and 1 atm.^c Mercury balance does not include liquid and solid effluents.

series could result in mercury removals of 99% or more [23]. Tables 7 and 8 show the cost estimates prepared by the Parsons–GTI group. A sensitivity analysis was performed on the most important factors affecting the economics, which is shown in Table 7, by varying these factors within a range of 50–200%. The study showed that combusting blends of coal with waste stocks, such as municipal solid waste (MSW), would double the concentration of mercury in the flue gas. However, the efficiency of the system would result in a cost/lb of mercury removed that was approximately one-third of the cost of removing the lower concentration produced from coal alone.

While cold-gas-cleaning technologies may offer effective removal of unwanted pollutants, the overall efficiency of the systems is lowered when the flue gas is cooled to below 300 °F (150 °C). However, in ignoring this penalty, the cost of mercury control can be relatively low. Both standard AC and treated AC beds can be effectively used and are commercially available at present. Both treated and untreated AC in a cold-gas IGCC system provide fairly long-term mercury removal, requiring bed material replacement only every 1.5–2 years. The Parsons–GTI study indicated that the sorbent beds were changed out, not because of reduced mercury loading, but to remedy one of three other potential problems: buildup in pressure drop, accumulation of water in the beds, or a

buildup of contaminant levels other than mercury. As noted above, even after 18 months of use, the study showed the packed sorbent beds only contained 9.6 wt% mercury.

Economic evaluations performed by the Parson–GTI study proved that mercury removal from an IGCC system that applies cold-gas cleanup technologies is significantly less expensive than mercury removal with the same feedstock in a pc-fired unit. Based on the 2002 estimates, effective mercury removal can be achieved for approximately US\$0.254/MWh. This equates, for this example case, to approximately US\$3412/lb of mercury removed—significantly less expensive than a pc-fired unit of the same size. However, costs are expected to be significantly higher for systems requiring hot- and warm-gas cleanup.

In contrast to cold-gas cleanup, hot-gas cleanup technologies involving mercury removal from IGCC systems are not sufficiently mature at this time, although it will become a potential option for the near term. In a hot- or warm-gas cleanup system, mercury must be removed from the generated syngas either before the gas turbine or from the flue gas exiting the turbine. To date, most efforts have focused on removal prior to the gas turbine. Data from tests conducted at conventional power plants show that sorbents can be temperature-sensitive, making mercury removal at high/warm-gas cleanup temperatures more of a challenge.

Table 7

Sensitivity of key parameters, US\$ on 2002 basis [27].

Capital costs factor	0.50	1.0	2.0
Total cost (US\$/MWh)	0.205	0.254	0.353
Mercury removal costs (US\$/lb)	\$2754	\$3412	\$4728
Carbon cost factor	0.50	1.0	2.0
Carbon costs (US\$/lb)	\$3.22	\$6.43	\$12.86
Total cost (US\$/MWh)	0.192	0.254	0.378
Mercury removal costs (US\$/lb)	\$2581	\$3412	\$5075
Carbon replacement factor	0.5	1.0	2.0
Carbon replacement time (months)	9	18	36
Total cost (US\$/MWh)	0.383	0.254	0.190
Mercury removal costs (US\$/lb)	\$5139	\$3412	\$2549
Mercury removal (%)		90	99+
Total cost (US\$/MWh)		0.254	0.393
Mercury removal costs (US\$/lb)		\$3412	\$4791

Table 8

Cost estimate for mercury removal by fixed carbon bed [23].

Plant parameter	Value
Plant net capacity (MWe)	250
Mercury level before fixed bed	52 ppbw
Mercury level after fixed bed	5 ppbw
Capacity factor	80%
Capital cost (US\$)	US\$ – 2002 values
Purchased equipment (PE) ^a	407,000
Installation ^b	203,500
Indirects ^c	122,100
Contingency ^d	101,750
Total capital costs (TCC)	834,350
TCC (\$/kW)	3.34
Operating and maintenance cost (US\$/year)	US\$ – 2002 values
Operating labor ^e	4380
Supervision ^f	657
Maintenance labor ^g	2409
Maintenance materials ^h	8344
Carbon ⁱ	217,203
Power ^j	36,792
Disposal ^k	8445
Overhead ^l	9080
Taxes, insurance, administration ^m	33,374
Total O&M	320,683
Capital recovery ⁿ	125,153
Total US\$/year	445,836
Total US\$/MWh	0.254
Mercury removal (lb/year)	131
Mercury removal cost (US\$/lb)	3412

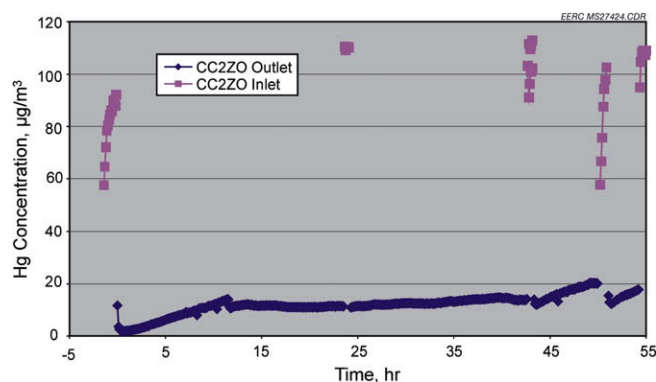
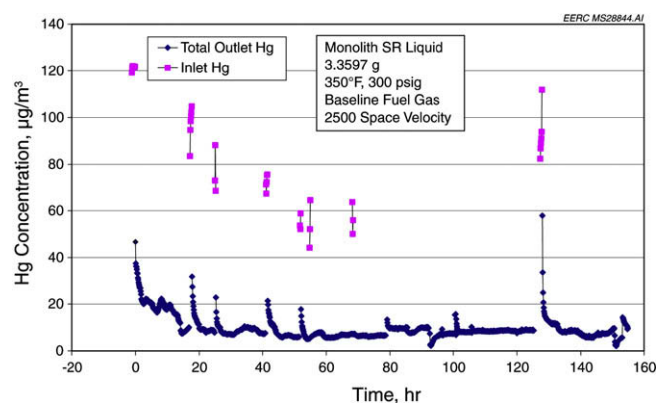
^a Scaled from Parson's in-house data.^b 50% of PE costs.^c 30% of PE costs.^d 25% of PE costs.^e 1 h/shift at US\$20/h.^f 15% of operating labor costs.^g 0.5 h/shift @10% wage rate premium over labor wage.^h 1% of TCC.ⁱ Based on calgon carbon corporation list price of US\$6.43/lb for sulfur-impregnated carbon.^j Using a pressure drop of 10 psi and 35 mils/kWh.^k Based on hazardous waste disposal of US\$500/ton.^l 60% of labor and maintenance costs.^m 4% of TCC.ⁿ Capital recovery factor of 15%.

Further development of newer sorbents has been very favorable. Work under way at the EERC and elsewhere has shown that treated ACs show greater mercury removal capacity than previously obtained using standard carbons. Continued development of these treated carbons is expected to yield reductions sufficient to meet commercial application within the next 1–3 years if results continue to be promising and other issues do not arise.

The EERC has been testing various sorbent materials and additives in a simulated laboratory-scale gasifier unit in order to find

solutions for cleanup of Hg, Se, and As [28]. Of particular interest have been several monoliths made by Corning, both with and without proprietary EERC treatments. Previous testing with a treated granular carbon showed good capture at 500 °F (260 °C); however, breakthrough occurred quickly. More importantly, over 90% of the Hg that was captured desorbed immediately after breakthrough, also releasing 90% of the treatment additive to the flue gas. By lowering the simulated flue gas temperature to 350 °F (177 °C), the treated granular carbon collected mercury much better and did not appear to desorb mercury. While the treated granular carbon appeared to be somewhat effective at capturing mercury at low-temperatures (~350 °F [180 °C]), the monoliths that the EERC tested appeared to work even better and for longer periods of time. For example, Fig. 2 shows results from a monolith (Test 18) coated with an improved additive, indicating a high degree of Hg capture for an extended period of time. For a short time period, the outlet mercury concentration was reduced to less than 5 µg/m³, which is roughly equivalent to the 5 ppbw goal for mercury emissions. Another EERC-treated Corning monolith (Test 36) using a less volatile form of an EERC additive showed high mercury capture at 350 °F (180 °C) without major desorption of the additive. A test at 500 °F (260 °C) with the same additive showed a diminishment in the length of time for mercury capture but no apparent desorption of mercury.

Fig. 3 shows results of another Corning-treated monolith using a different additive formulation. These results show effective capture of mercury for over 150 h of testing at 350 °F (180 °C). This monolith-additive combination was also tested at pressures up

**Fig. 2.** Breakthrough curve for EERC-treated monolith (Test 18 – CC2ZO) at 350 °F (177 °C).**Fig. 3.** Breakthrough curve for Corning-treated monolith (Test 41 – SR Liquid) at 350 °F (177 °C).

to 600 psig and temperatures up to 700 °F (370 °C) and was found to be very effective.

6. Conclusion

Worldwide, mercury is an issue that coal-fired electric power producers are required to address. Several mercury control technologies are in various stages of development, with the most mature technology being AC, plain or treated. While treated and nontreated ACs have been demonstrated to be effective at a number of conventional coal combustion power plants, there are many plants at which ACs have not performed well, such as plants that have high-sulfur (SO₂ and SO₃) emissions and gasification systems that employ hot- and warm-gas cleanup. When treated and nontreated ACs have proven effective, mercury removal efficiencies have exceeded 50% and, in many cases, approached 90% capture. However, for other tests and/or at other plants, capture has been below 30%. Consequently, there is not one single technology that can be applied to effectively control mercury at all plants. Plant type (pc-fired, oxycombustion, gasification, etc.), configuration, operating characteristics, coal rank, flue gas chemistry, etc., are unique to each plant and need to be considered when appropriate mercury control technologies are developed and/or evaluated. A number of technologies are under development and show promise for effective mercury control and commercial viability. These technologies are more developed and demonstrated for conventional coal combustion power plants, with more understanding, test data, and technology options needed for advanced power systems, such as oxycombustion and gasification. Although pc-fired power plants are most common throughout the world, advanced systems including ultrasupercritical and FBC, oxycombustion, and gasification technologies are of particular interest because of energy efficiency and CO₂ concerns. Consequently, effective mercury control technologies are needed to permit use of these advanced systems.

Disclaimer

This report was prepared as an account of work fully or partially sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any other sponsors of the work makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Furthermore said sponsors do not assume any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this article. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any other sponsors of the work. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any other sponsors of the work.

Acknowledgments

The authors wish to acknowledge several organizations for their significant support of coal-fired generation at the Energy & Environmental Research Center, including the US Department of Energy's National Energy Technology Laboratory, the US Environmental Protection Agency, the North Dakota Industrial Commission, the Elec-

tric Power Research Institute, and many other entities that have allowed us the opportunity to further advancements in this area.

References

- [1] Revision of December 2000 Regulatory Finding on the Emissions of Hazardous Air Pollutants from Electric Utility Steam Generating Units and the Removal of Coal- and Oil-Fired Electric Utility Steam Generating Units from the Section 112(c) List; Final Rule (Clean Air Mercury Rule [CAMR]). Code of Federal Regulations; 40 CFR, Part 63, Fed Regist 2005;70 (59):15993.
- [2] US Environmental Protection Agency. Rule to Reduce Interstate Transport of Fine Particulate Matter and Ozone (Clean Air Interstate Rule); Revisions to Acid Rain Program; Revisions to the NO_x SIP Call; Final Rule. Fed Regist 2005;70:91.
- [3] Pavlish J. Understanding mercury speciation, variability, and operational impacts on mercury control. In: 8th international conference on mercury as a global pollutant; August 2006.
- [4] US Environmental Protection Agency. A Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units: Final Report to Congress; EPA-453/R-98-004a; US EPA Office of Air Planning and Standards. US Government Printing Office: Washington, DC; 1998.
- [5] US Environmental Protection Agency. Mercury Study Report to Congress; EPA-452/R-97-003; US EPA Office of Air Quality Planning and Standards. US Government Printing Office: Washington, DC; December 1997.
- [6] Miller PJ, Atten CV. North American Power Plant Emissions. www.cec.org/files/PDF/POLLUTANTS/PowerPlant_AirEmission_en.pdf [accessed January 2005].
- [7] Valupadas P. Mercury emissions regulation for coal-fired power plants. In: Proceedings of air quality VI: mercury, trace elements, SO₃, particulate matter, and greenhouse gases conference, Arlington, VA, September 24–27; 2007.
- [8] United Nations Environment Programme, Chemicals Branch. The global atmospheric mercury assessment: sources, emissions, and transport. UNEP: Geneva, Switzerland; December 2008.
- [9] Felsvang K, Gleiser R, Juip G, Nielsen KK. Air toxics control by spray dryer absorption systems. In: Proceedings of the 2nd international conference on managing hazardous air pollutants, Washington, DC, July 13–15; 1993.
- [10] Weyland B. EPA's mercury programs: an update. In: Proceedings of air quality VI: mercury, trace elements, SO₃, particulate matter, and greenhouse gases conference, Arlington, VA, September 24–27; 2007.
- [11] Jones AP, Hoffmann JW, Smith DN, Feeley III TJ, Murphy JT. DOE/NETL's Phase II Mercury Control Technology Field Testing Program: Preliminary Economic Analysis of Activated Carbon Injection; Report for US Department of Energy Office of Fossil Energy National Energy Technology Laboratory Innovations for Existing Plants Program; April 2006.
- [12] US Environmental Protection Agency, Information Collection Request; 1999.
- [13] Benson SA, Jones ML, Nyberg CM, Crocker CR, Hajicek DR, Henderson AK, et al. Assessment of Mercury Control Options and Ash Behavior in Fluidized-Bed Combustion Systems; Final Report (January 1, 2005 – September 2007) for US Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40321; EERC Publication 2007-EERC-10-05. Energy & Environmental Research Center: Grand Forks, ND; October 2007.
- [14] Zheng L, Furimsky E. Assessment of coal combustion in O₂ + CO₂ by equilibrium calculations. Fuel Process Technol 2003;81:23–34.
- [15] Varhegyi G, Szabo P, Jakab E, Till F. Mathematical modeling of char reactivity in Ar–O₂ and CO₂–O₂ mixtures. Energy Fuel 1996;10:1208–14.
- [16] Varhegyi G, Till F. Comparison of temperature-programmed char combustion in CO₂–O₂ and Ar–O₂ mixtures at elevated pressure. Energy Fuel 1999;13: 539–40.
- [17] Shaddix CR, Murphy JJ. Coal char combustion reactivity in oxyfuel applications. In: 20th Pittsburgh coal conference; 2003.
- [18] Croiset E, Thambimuthu KV. NO_x and SO_x emission from O₂/CO₂ recycled coal combustion. Fuel 2001;80:2117–21.
- [19] Okazaki K, Ando T. NO_x reduction mechanism in coal combustion with recycled CO₂. Energy 1997;2:207–15.
- [20] Suriyawong A, Gamble MD, Lee M, Axelbaum RL, Biswas P. Submicrometer particle formation and mercury speciation under O₂–CO₂ coal combustion. Energy Fuel 2006;20:2357–63.
- [21] Hu Y, Naito S, Kobayashi N, Hasatani M. CO₂, NO_x, and SO₂ emissions from the combustion of coal with high oxygen concentration gases. Fuel 2000;79: 1925–32.
- [22] Sondreal EA, Swanson ML, Benson SA, Holmes MJ, Jensen MD. A review of gasification technology for coproduction of power, synfuels, and hydrogen from low-rank coals. In: Proceedings of the 20th symposium on western fuels: international conference on lignite, brown, and subbituminous coals, Denver, CO, October 24–26; 2006.
- [23] Granite EJ, King WP, Pennline HW. Techniques for mercury control and measurement in gasification systems. In: Presented at the 5th international symposium on gas cleaning, Morgantown, WV; September 2002.
- [24] Newby RA, Lippert TE, Slimane RB, Akpolat OM, Pandya K, Lau FS, et al. Novel Gas Cleaning/Conditioning for Integrated Gasification Combined Cycle; Final Report to US Department of Energy for Contract No. DE-AC26-99FT40674; Siemens Westinghouse Power Corporation, Pittsburgh, PA, and GTI, Des Plaines, IL; 2001.

- [25] Pflughoeft-Hassett DF. IGCC and PFBC By-Products Generation, Characteristics, and Management Practices; EERC Final Report to US Environmental Protection Agency; Final Report No. 97-EERC-09-06; September 1997.
- [26] Ratafia-Brown J, Manfredo L, Hoffmann J, Ramezan M. Major Environmental Aspects of Gasification-Based Power Generation Technologies; Science Applications International Corporation. Final Report for Gasification Technologies Program; National Energy Technology Laboratory, US Department of Energy; December 2002.
- [27] Rutkowski MD, Klett MG, Maxwell RC. The cost of mercury removal in an IGCC plant. In: Presented at gasification technologies 2002, San Francisco, CA, October 27–30; 2002.
- [28] Musich MA, Swanson ML, Dunham GE, Tennant J, Kuang P, Johnson B, et al. Advanced mercury and trace metal control with monolith traps. In: Presented at 2007 Pittsburgh coal conference, Johannesburg, South Africa, September 10–14; 2007.