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Review

Mercury flow via coal and coal utilization by-products: A global perspective

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Abstract

Mercury (Hg) has been known to society and used since ancient times. The metal has drawn considerable attention and concern due to its toxicity, persistence, bioaccumulation and long range transport in the atmosphere after emission from coal-fired utilities as well various other high temperature processes. Coal is an important fuel for the production of heat and electricity and in recent years annual hard coal production has approached a level of around 5000 million metric tonnes (Mt, t = 1000 kg). Global Hg flows via coal and coal utilization by-products (CUBs) are presented in this paper, which are important in light of the regulations to limit the global emissions of Hg and its cycling as well as its circulation via coal and the CUBs. There are no detailed statistics on the global production and consumption of coal fly ash (FA) and in this study, we have estimated the total global FA production for the year 2003 based on ash content in coals and typical flue gas control technology for pulverized coal combustion. The mode of occurrence and concentration of Hg in coal and coal FA for different countries have been evaluated and presented in this study. The total Hg amount in coals processed worldwide was found to be 1534 t in 2003 based on a global average concentration of 0.3 mg/kg in coal. In addition, "hidden" flows of Hg through export and import of coal assessed during this study, add up to about 149 t. In this study, the economic uses of the FA in different sectors such as cement industry, agriculture, land reclamation, filers for asphalt, plastic and many others have been discussed in details. However, there is not much information on uses of coal FA in the developing countries. In the final part of the paper, a short survey has been focused on a few coal producing countries including Australia, China, EU-states, India, Japan, Korea, Russia, South Africa and South American countries, addressing the status of coal and coal FA use and the fate of the Hg that is mobilized.
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Keywords: Mercury; Coal; Coal fly ash; Material flow; Uses of fly ash; China, India, and a few other countries

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1. Introduction

In the environment most changes are brought by natural and anthropogenic processes that affect material and energy flow. It is necessary to account for material flows in economies and environment so that appropriate information can be provided to decision-makers, resource users and engineers for better understanding and quick actions that will maximize resource use and minimize the adverse environmental and health impacts (Schaltegger and Burritt, 2000). The flow of trace metals, metalloids and organic compounds occur through raw materials mined from the Earth or through a manufactured product, but the effects of these trace elements left in nature can be profound. It is therefore necessary to understand the whole set of trajectories for materials flow for trace elements from extraction to end use. Since the past decade, investigations have been undertaken to study the effects of material flow on economy, society and the environment and the importance of the use of various material in a sustainable manner so that impacts on the ecosystem and the people are minimal (ETC/RWM, 2006; Hilliard, 1994; Loebenstein, 1994; Mukherjee et al., 2004; USGS, 1998).

During the course of geological history, increasing temperature and pressure spanning over millions of years, the plant material and peat bogs have been converted to lignite, sub-bituminous coal, bituminous coal and anthracite. Today coal is a major source of energy in developed as well as developing countries and it will continue to be a major source of heat and electricity until the middle of the 21st century (Finkelman et al., 2002; Reichel, 2003). The demands for all resources are expected to increase with increasing population. This is particularly true for the fossil fuel such as coal that is needed for electricity and heat generation. It is anticipated that in many countries alternative energy supply options will be needed for national security as well as to fulfill the requirements of international agreements such as the 1997 Kyoto Protocol (Mills, 2004).

Knowledge of the presence and mobilization of potentially harmful trace elements in coal and coal

utilization by-products (CUBs)[1] is essential for decision-making regarding the controlled management of toxic substances, associated with coal and the CUBs. Material flow analysis (MFA) can be employed to detect the links between environmental problems and human activities. Metal flow through raw materials and products, their use, reuse, disposal and recycling are vital for a country to ensure sustainable national, regional and global economic development (Mukherjee et al., 2000; Sznopek and Goonam, 2000).

Mercury (Hg) is one of the most toxic elements in coal and the CUB that is cycled both in the terrestrial and aquatic environments on regional and global scales (Foley and McKay, 2000; Schroeder and Munthe, 1998). During the past five centuries, about 923 kt (kilo tonnes) of Hg has been extracted from cinnabar (HgS), and also as by-products during the processing of other metal production (Wong et al., 2006). Based on the annual consumption of about 4 Mt in a power plant with a capacity of 1000 MW (Gabbard, 1993) the world consumption of coal for the year 2040 is projected to be more than 12,500 Mt (million metric tonnes). Extensive efforts have been made to evaluate the Hg emissions from coal-fired power plants as well as from coal FA dumped near a coal-fired power plant in order to assess reduction strategies for Hg pollution from coal (Mukherjee and Zevenhoven, 2006; Yudovich and Ketris, 2005a,b). Global Hg emissions were reviewed for the year 2000 in detail by Pacyna et al. (2006) and it was observed that two thirds (1.46 kt) of the total atmospheric emission (2.19 kt) originate from coal combustion. Estimation of Hg emission from Chinese stationary coal-fired power plants was found to be 220 t for the year 2000 (Jiang et al., 2005; Zhang and Wong, 2007). These emissions were specified as around 16% elemental Hg vapor (Hg^0), around 23% as particle-bound (Hg-p), and around 61% as oxidized vapor species Hg^{2+} (Streets et al., 2005, see also Section 4 below). In a recent document[2] (USEPA, 2005a), a 40% reduction of Hg emission from coal combustion in utility boilers by 2010, and another 70% reduction by 2018 (USEPA, 2005b) for the benefit of humans, animals, plants and especially aquatic species. Due to the volatile and persistent nature of Hg volatility, persistency and bioaccumulation as methyl-mercury (Me-Hg) poses a great threat to public health, primarily via contaminated fish (Finkelman et al., 2002; Lindberg et al., 2004; López-Antón et al., 2006; Merger et al., 2007).

There is a good overview of worldwide production and consumption of coal (World Coal Institute, 2006), but unfortunately there are few detailed studies on production and consumption of CUBs and their use pattern on a regional and global basis. In addition, there is scant information on the behaviors and fate of trace elements in CUBs in soils with different properties, such as pH, organic matter, salinity as well as trace elements and organic compounds present in the soil. Hence, considerable information gaps exist in the area of: (i) the science and technology of Hg emission control at coal combustion plants, (ii) the chemistry of the CUBs, (iii) their use pattern and handling regulations, and (iv) its safety in the environment.

The present study is based on literature survey aiming at mapping scattered data on the occurrences, production, consumption, use patterns, and flow of Hg in coal and CUBs, on the global basis. Several calculations were made in this study as to generate data of a more informative character. We have tried to highlight the problems of Hg linked to coal through extraction and production of coal, its uses, import and export. The major emphasis of this review is on (a) patterns of Hg concentration in coal and FA; (b) flow of Hg through coal and coal products; (c) behavior of Hg during coal combustion; (d) the pattern of the use of coal FA. In addition, case studies have been discussed for China and India regarding Hg flow through coal and the CUBs and its effects on the Chinese and Indian ecosystems. Improved Hg control technology should be selected and recently EPRI (Electric Utilities, and Research Organization) has developed a method such as sorbent injection technology for Hg control (Chang, 2000). Coal utilization by-products (e.g. FA, bottom ash and slag, fluidized combustion bed materials, and FGD residues) should be used thoughtfully because some of these materials, such as FGD scrubber materials contain high concentration of Hg (39–70 μg/g) (DeVito and Rosenhoover, 1999).

In this study, we have also touched upon scenarios of coal and CUBs for Australia, the new EU-27 member states, Japan, Korea, Russian Federation, South Africa and several South American countries.

2. Coal production and consumption

2.1. Overview

Fossil fuel power plants contribute 40% of the world's energy and in 2004, the world total hard coal produc-

[1] National Energy Technological Laboratory (US Department of Energy) (DoE/NETL) claims "Utilization" is a broader term than "Combustion" because coal gasification generates other varieties of solid materials than coal combustion (Aljoe et al., 2005).

[2] U.S. Clean Air Interstate Rule (USEPA, 2005a).

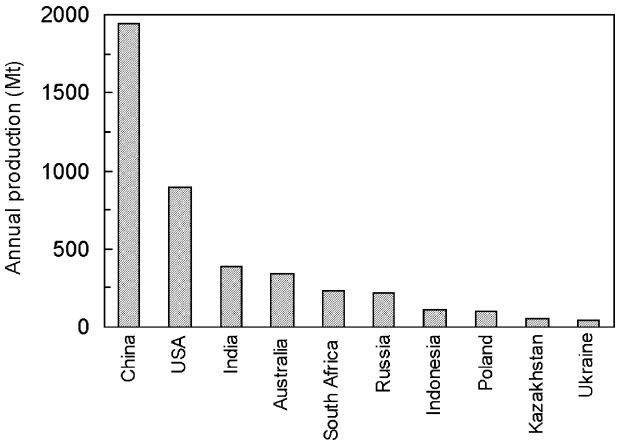


Fig. 1. Hard coal production for 10 countries, 2004 (Mt). World Coal Institute (2006).

tion reached at 4600 Mt whereas lignite coal production was at 893 Mt and in 2005 global brown coal production was 905 Mt (World Coal Institute, 2006). Fig. 1 indicates production of hard coal for 10 important coal producing countries in the world. Global total recoverable reserves of coal have been estimated at 984,453 Mt (BP, 2003) as shown in Table 1. This recoverable reserves are available in around 70 countries with the largest deposits are in the United States followed by the Russian Federation, and China (Barnes and Sear, 2004) For 2030, global production of hard coal is expected to reach 7000 Mt. The largest producers of hard coal are China, the United States, India, Australia and South Africa (World Coal Institute, 2006). Between 1997 and 2002 the reduction of hard coal production was 69%, i.e. 271–187 Mt in the EU-15 countries. A few EU countries such as Germany, the United Kingdom and Spain still produce significant amount of hard coal (Mills, 2004). In South America,

Table 1
Global reserves of coal, 2002 (Mills, 2004)

Country	Coal in million metric tonnes	In %
USA	249,994	25.4
Russian Federation	157,010	15.9
China	114,500	11.6
India	84,396	8.6
Australia	82,090	8.3
EU-15	71,677.5	7.3
EU-10 accession countries	29,381.3	2.98
Total world coal reserves	984,453	

the major coal deposits are on the west side of the continent. In 2004, South America represented only 1.3% of world's coal production (Tewalt et al., 2007).

World annual coal consumption has increased from 2780 Mt in 1980 to current levels that approach 5000 Mt. The maximum consumption was in the following order in 2004: Asia (2610 Mt) > China (1700 Mt) > North America (1050 Mt) > others (540 Mt) > Europe > (400 Mt). With the increased production of coal, and the release of Hg from coal-fired utility boilers, it is possible to determine the mean Hg concentration in coal and its by-products (i.e. CUBs) for each region and how many million tonnes of Hg is relocated when coal is exported or imported. A coal flow chart (Fig. 2) predicts how Hg flows along with coal.

2.2. Coal utilization by-products

Coal utilization by-products are produced during the combustion and gasification of coal and are broadly divided into FA, bottom ash, boiler slag, gasifier ash

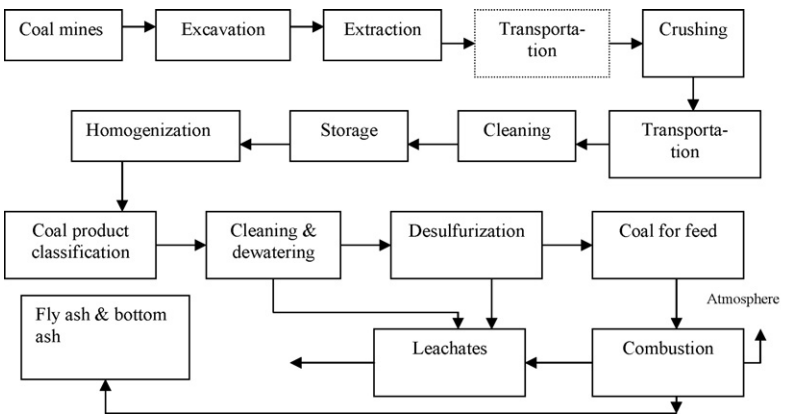


Fig. 2. Mercury flows through coal from mines to the combustion chamber for the production of heat and electricity. We assume that there is no change of Hg during flows, but it will leach from dewatering and desulfurization processes. Some parts will enter into the atmosphere from the combustion and the rest will enter into fly ash and bottom ash (modified from González Cantú, 2005).

Table 2
Fly ash production from coal combustion in utility boilers in selected regions of the globe

Country/region	Production (Mt)	Year	References
Australia	12.4	2003	Wang and Wu (2006)
Canada	7.0	1999	Kalyoncu (2002)
China	160	2002	Koukouzas et al. (2006)
EU-15	44.2	2003	Vom Berg and Feuerborn (2005)
India	89.6	2000	Mukherjee and Zevenhoven (2006)
Israel	0.735; 1.1	1995; 2001 (estimated)	Foner and Robb (1997)
Japan	9.1	1999	Kalyoncu (2002)
South Africa	30	2003	Eskon Annual Report (2006)
USA[a]	76.5	2002	The Fly Ash Resource Center (2005)
Total	430		
World	413.7	2003	This study

[a] In the United States CUBs were produced 122 Mt in 2004 (Xin et al., 2006).

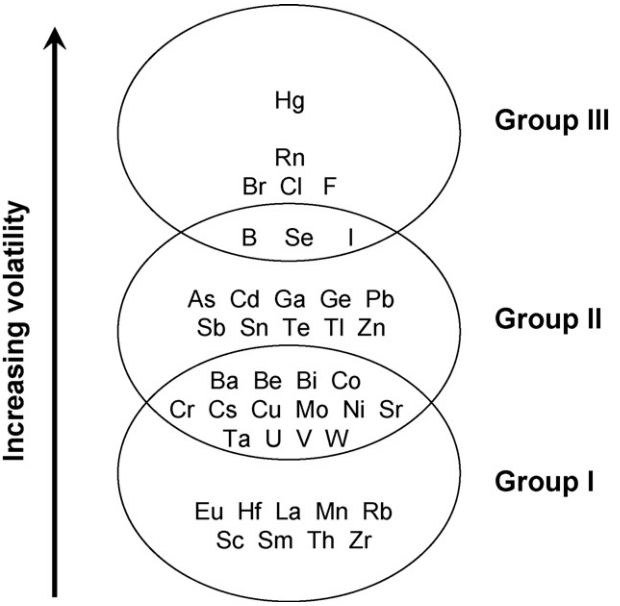


Fig. 3. Classification of trace elements during combustion and gasification (reproduced from Clarke and Sloss, 1992).

and slag, and flue gas desulfurization (FGD) solids. All these by-products contain Hg and other trace elements. As for coal FA there is scarce information on accurate statistics for production and consumption of these products in different regions of developing countries, but in the developed regions information are available (Table 2). Based on the Resource Conservation and Recovery Act (RCRA) (Aljoe et al., 2005), the CUBs have been classified as a non-hazardous solid product by the US Environmental Protection Agency (USEPA). In most countries, coal FA is not regarded as a hazardous waste, but is identified as a waste yet not considered a secondary raw material (Riely, 2006) that can be offered to the market. In this review, we consider mainly pulverized coal combustion FA. Such fly ashes consist mainly of aluminosilicate glass, mullite ($Al_6Si_2O_{13}$) silica (SiO_2), magnetite (Fe_3O_4), anorthite/albite [(Ca, Na)(Al, Si_4)O_8], anhydrite ($CaSO_4$), ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$), opal ($SiO_2$), iron oxide ($Fe_2O_3$), and in varying amounts lime (CaO) (Moreno et al., 2005). The chemical composition and physical properties of FA depends very much on: (a) composition of coal and its source; (b) burning condition and temperature of the boiler; (c) boiler configuration; (d) the particle size of coal; (e) the gas cleaning equipment (R. Finkelman, personal communication, 2002).

In addition, the FA also contains much of the trace elements that are generally found in coal. These toxic elements are mainly in volatility groups II and III (Fig. 3) based on the chemistry and the volatilization–condensation mechanism of particles during coal combustion in power utility boilers (Clarke and Sloss, 1992; Meij, 1991). In this review, total CUBs has been estimated at 591 Mt of which 25% bottom ash, 5% boiler slag and 70% coal fly ash (see Fig. 4), and based on an average ash content in bituminous coal (12.0%), the world total FA production for 2003 was estimated at 413.7 Mt of which about 20 Mt enter into the atmosphere (see Fig. 4). However, it must be noted that in several countries (such as in China), there is no gas cleaning equipment in many small and large coal-fired power plants. In general, the efficiency of electrostatic precipitator (ESP) and fabric filters (FFs) to separate particulates from the gas stream is 99% whereas wet scrubbers have somewhat lower separation efficiency (Clarke and Sloss, 1992). The European Coal Combustion Byproducts (ECOBA) has estimated the world production of FA was approximately 480 Mt in 2000: China: 100 Mt; India: 80 Mt; Russia: 50 Mt; Eastern Europe 45 Mt; South Africa: 30 Mt; North America: 83 Mt; Europe (EU-15): 47 Mt; others: 45 Mt (Barnes and Sear, 2004).

In our study, the estimated 393 Mt of FA (see Fig. 4) may be used as raw material for various industrial products as well as liming material in agricultural, because FA acts similar to lithospheric (soil-like) materials. Asokan et al. (1996) estimated in their study the global release

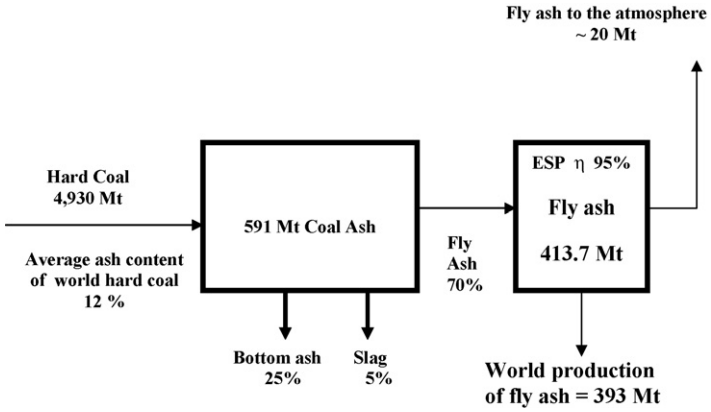


Fig. 4. Estimated global fly ash production, 2003.

of coal combustion residues (slag, FA, bottom ash, and fluidized bed combustion ash) to be about 520 Mt (our study estimates 591 Mt of CUBs for 2003). It should be stressed here that FGD-ashes from dry and semi-dry processes may have considerable effect on the end product properties due to pH, forms of sulfur, and calcium compounds as well as presence of trace elements (Twardowska, 1999). In this study, the FA production and consumption data were found for Australia, Canada, China Europe, India, Israel, Japan, Korea, Russia, South Africa, and the United States (Table 2). No values have been reported for South American coal FA.

3. Mode of occurrence and concentration of mercury in coal and coal fly ash

3.1. Mercury in coal

The occurrence and concentration of trace elements in coal has been studied by several researchers (Clarke and Sloss, 1992; Finkelman, 1989, 2003; Kolker et al., 2006; Swaine, 1990; Yudovich and Ketris, 2005a). This information is valuable to develop strategies to reduce these elements' mobilization in air, water and land as a result of coal combustion, during mining of coal or disposal or use of by-products. Mercury and other trace elements can exist in coal as organic and inorganic components. Mercury is a chalcophile element, e.g. with great affinity to sulfur-containing components in coal. Mercury is generally incorporated in pyrite and the proportion of Hg varies with mineral paragenesis (Kolker et al., 2006). It is known that during coal cleaning processes, it is also possible to remove substantial amounts of Hg and arsenic as they occur in coarse-grained pyrite (Finkelman, 1994). This generally correlates with low rank coals such as lignite and sub-bituminous coal, which contain significant carboxylic and phenolic hydroxyl groups (Swaine, 1990). However, studies on the determination of Hg in organic matter in coal are quite limited (Kolker et al., 2006).

The modes of occurrence or speciation of Hg and other trace elements in coal can be measured by different processes including: (a) sink-float data; (b) statistical correlation with other trace element or coal ash; (c) geochemical characteristics; or (d) from the behavior during heating or leaching of coal (Finkelman, 1994; Palmer et al., 2002). There are many leaching methods (Hesbach and Lamey, 2001 *vide* Kim, 2002) from which a proper method should be selected based on pH, redox potential of the environment, nature of FA, chemical form of the element and its concentration on the surface of the ash (Riely, 2006). The tests generally focus on the potential release of trace elements to the specific surface or groundwater environments where ash should be applied. However, leaching tests may also indicate the suitability of a product such as FA as a soil amendment (Nakurawa et al., 2003; Sloss, 2007).

Mercury concentration in coal varies from mine to mine. Higher concentration (>1.0 mg/kg) is quite rare, but many authors cited higher values for coal. This high concentration of Hg in coal is due to natural geological processes. We have collected data for Hg concentration in coal for nine coal producing countries and five less important coal producing regions in South America (Table 3). Many authors (Diehl et al., 2004; Finkelman, 2003; Kolker et al., 2006; Park et al., 2006; Quick et al., 2003) and organizations (CCME, 2005; USEPA, 2002) have presented and discussed Hg data for anthracite, bituminous and lignite coals. The concentration of Hg measured in coal depends on: (a) density (b) presence of sulfur, and (c) analytical technique. Moisture of whole coal must be determined correctly for better Hg results

Table 3
Range of mercury concentrations (mg/kg) in coal and coal fly ash[a] from different geographical regions

Country/region	Hg in coal	Hg in coal fly ash
Australia	0.01–1.0	0.34
China	0.19–0.303; 0.15[b]	–
Guizhou Province	0.52	–
Europe	0.01–1.5	0.23
India	0.11–0.80	0.007–0.28
India (by NTPC)[c]	0.11–0.14	
Japan	0.045	–
Korea	0.012–0.048	–
Russia	0.02–0.9	
South Africa	0.01–1.0	0.56–0.64
South America[d]		
Argentina	0.021–0.96[e] ($n = 7$)	
Brazil	0.041–0.778[e] ($n = 57$)	
Colombia	0.020–0.17[e] ($n = 16$)	
Peru	0.041–0.63[e] ($n = 16$)	
Venezuela	0.030–0.280[e] ($n = 16$)	0.268
USA	0.17 (mean)	
World	0.02–1.0	0.62

[a] Summarized from various sources.
[b] Based on 305 samples; Belkin et al. (2006).
[c] NTPC: National Thermal Power Corporation, India.
[d] Karlsen et al. (2006).
[e] Dry whole coal basis.

in coal. Park et al. (2006) analyzed Hg in different coals from different countries (Korea, Australia, China, Indonesia, and Russia). When coals have high density, e.g. are buried deep in the ground they often contain a high concentration of Hg. In their study anthracite coals were found to have higher a density (2.0–2.2 g/cm^3) than bituminous coals (1.4–1.7 g/cm^3). Mercury concentration of Korean anthracite coals varied between 434.5 ± 2.1 ng/g and in bituminous coals from Australia 15.6 ± 2.8 ng/g. Their study also indicated analytical techniques, e.g. acid extraction and pyrolysis will provide different results for the same type of coal. There are different opinions on sulfur content and Hg concentration in coal. Yudovich and Ketris (2005a) believed that high sulfur content in coal will raise the Hg concentration, but studies by the USEPA (1998) indicated that there is no relation between high Hg concentration and sulfur content in coal. There are many parameters such as carbon content and moisture that may affect Hg concentration in coal. Hence, our knowledge on the chemistry of Hg in coal is still lacking.

Dai et al. (2006) studied the mode of occurrence of Hg in coals from Southwest China. The reported Hg concentration of coals from Shimenkan and Xingren (China) was 12.1 mg/kg. Minor quantities of Hg (0.08 wt.%) have also been reported in getchellite ($AsSbS_3$) in coal, but the mode of occurrence of Hg in pyrite, syngenetic kaolinite, and organic matter could not be measured because it was below the detection limit (Dai et al., 2006).

South African coals (high yield coals) contain low levels of Hg which often correlates with lower concentrations of sulfur (0.02–1.23 wt.%) as well when compared to coals from the northern hemisphere (Wagner and Hlatshwayo, 2005). The association of Hg in these coals is not only with pyrite but it can be also with sphalerite and organic components (WVGES, 2002).

3.2. Coal fly ash

It has been assumed that 70% of the ash-forming matter in coal enter into FA when coal is burnt in the utility boiler, where as Jankowski et al. (2006) reported 80% conversion for an Australian utility boiler. The general composition and properties of FA were discussed above (Section 2.2).

Pavlish et al. (2003) reviewed the Hg capture on the FA and concluded that Hg removal from the process is coal-dependent and also chlorine content in coal. There are different technologies available which give 50% capture of Hg for CS-ESP (cold-side electrostatic precipitator), 80% for FFs (fabric filters), 70% for CS-ESP followed by WFGD (wet flue gas desulfurization) while up to 99% separation of Hg may be obtained using spray dryer FGD combined with a FF. Due to physiochemical properties, Hg is released from coal at temperatures as low as 150–200 °C and the capture of Hg on FA increases as the gas temperature drops to below 400 °C as well as when the contact time between flue gas and the FA increases. The enrichment of Hg concentration on unburnt carbon in FA has been reported in many studies. It is well established that Hg tends to concentrate on the finer FA fraction of low and high quality of coal (Butz and Albiston, 2000; Hassett and Eylands, 1999), but its concentration varies in the different petrographic components found in the un-burnt carbon from hard/bituminous coal (Hower et al., 2000). It is necessary to understand how the volatile element Hg is associated with the FA because it might be used for purposes such as remediation, restorations, stabilization, cement production, and improvement of soil quality. Our estimations of the flow of Hg through the FA are based on the concentration of Hg in FA from different regions, although a few values were available for this study (see Table 3).

Table 4
Use pattern of coal combustion by-products (in Mt, million short tons[**]) in the United States, 2005 (ACAA, 2007)

	Total production					
	71.1	17.6	11.98	17.70	1.958	1.427
Application areas	Fly ash	Bottom ash	FGD gypsum	FGD material, wet scrubbers	Boiler slag	FGD material, dry scrubbers
Concrete	14.99	1.02	0.329	0	0	0.0139
Cement	2.84	0.94	0.397	782[*]	0.043	0
Flowable fill	0.089	0	0	0	0	0.0096
Structural fills	5.71	2.32	0	0	0.175	0.0027
Road/pavement	0.21	1.06	0	0	300[*]	0
Soil stabilization	0.72	0.21	0	0	0	0.0015
Mineral filler in asphalt	0.063	0.022	0	0	0.057	0
Snow and ice control	591[*]	0.53	0	0	0.015	0
Blasting/roofing	0	0.089	0	0	1.54	0
Mining	0.63	0.047	0	0.25	0.032	0.11
Wallboard	0	0	8.18	0	0	0
Waste stabilization	2.66	0.042	0	0	0	0
Agriculture	0.024	0.0076	0.362	0.003	0	0.019
Aggregate	0.18	0.69	0	0		
Others	1.02	0.57	0.0021	0.44	0.025	0
Total	29.13	7.54	9.27	0.694	1.887	0.157
Utilization rate	40.97%	42.84%	77.37%	3.92%	96.38%	11.00%

[**] 1 Short ton = 0.907 metric tons (mt).
[*] = short tons.

4. Utilization of fly ash

The proportion of coal FA use across the world amounts to only 15–20% of the total production (Clarke and Sloss, 1992; Manz, 1992). Utilization patterns vary form country to country. In the Netherlands 100% FA is used in different sectors. In the West, its use is maximal (except the U.S.), whereas in the developing countries rather negligible amounts are being utilized. In the US, Europe and Japan, FA is mainly used in concrete and cement manufacturing industries. Details on the use pattern of CUBs in the US are given in Table 4. Cement manufacturing is an energy demanding process where 80% of the energy is used for the conversion of raw feed into clinker. Fly ash with un-burnt carbon is useful as a raw material to compensate for a small part of the fuel in the cement production process. Table 5 shows different composition of oxides in different classes of FA.

Fly ash can also be used in the ceramic industry, in synthesis of high cation exchange capacity (CEC) zeolites, as additives for immobilization of pollutants in industrial and water treatment plants, mining areas for fillings, as sorbents for flue gas desulfurization, in slash (ash/sludge) production for soil amendment and it also stores toxic metals such as Al, Si, Fe, Ge, Ga, V, and Ni (Moreno et al., 2005). Wang and Wu (2006) showed the possible use pattern of FA in different sectors (Fig. 5) and summarized how this material can be used to reduce the environmental burden and enhance economic development.

Fly ash can be land applied in combination with other by-products such as sewage sludge or bio-solids to improve the physical properties of soils, e.g. decreased infiltration rate, lower bulk density as well as to overcome some nutrient deficiency in soils (Punshon et al., 2003).

Table 5
Oxide composition of three types of fly ash (wt.%) (reproduced from Bhatty and Gajda, 2005)

Oxides	Fly ash A	Fly ash B	Fly ash C	Shale[a] (typical)
SiO_2	42.95	47.87	52.50	56.53
Al_2O_3	15.46	17.08	21.62	15.06
Fe_2O_3	7.10	8.59	8.53	9.22
CaO	4.47	4.68	3.80	4.00
MgO	1.30	1.21	1.09	1.41
SO_3	0.49	0.21	0.48	0.09
Na_2O	1.88	2.02	1.15	0.12
K_2O	2.50	2.77	2.06	2.71
TiO_2	1.08	1.13	1.03	0.85
LoI[b] at 950 °C	20.83	12.97	6.91	9.51

[a] Oxide values of the material shale have been shown for comparison purpose and values are in wt.%.
[b] LoI, loss of ignition.

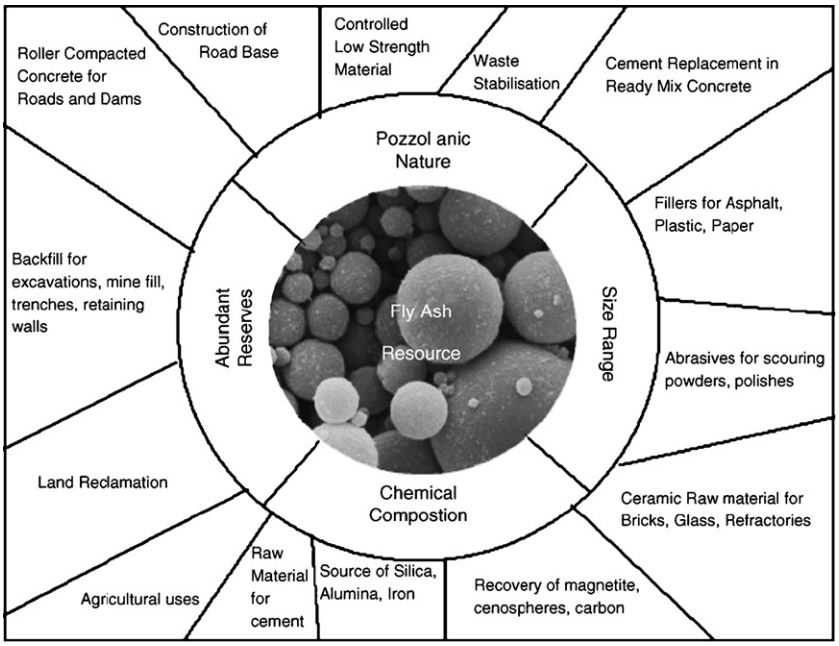


Fig. 5. Possible use pattern of Coal Fly ash (reproduced from Wang and Wu, 2006).

Due to versatile properties, FA can be used as an absorbent for NO_x and described the techniques to enhance the absorption chemistry by the presence of unburnt carbon in the FA (Lu and Do, 1991). Several other metal ions such as Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}, Cr^{6+}, Hg^{2+}, As^{3+}, As^{5+} and Cs^{+} can be removed from wastewaters by using FA precipitation and adsorption mechanisms. Precipitation of a metal occurs due to presence of calcium hydroxide in FA and adsorption may be enhanced due to association of silica and alumina in the FA (Gangoli et al., 1975; Lu and Do, 1991). In most cases, removal efficiency depends on metal concentration, pH and temperature (Grover and Narayanaswamy, 1982; Kelleher et al., 2002; Pandey et al., 1984; Sen and De, 1987).

Radionuclides of ^{137}Cs and ^{90}Sr are reported to be adsorbed by coal FA as cited by Apak et al. (1996). Kikuchi (1999) showed that zeolite can be used effectively for wastewater treatment and also as a desulfurizing agent for air purification. Chaturvedi et al. (1990) studied the use of coal FA to remove fluoride from wastewater and water by an adsorption method based on concentration, temperature and pH of the solution.

Many researchers have used FA to modify soil properties for better crop production. Fly ash contains mostly all elements for plant growth in varying concentrations except nitrogen (Keefer, 1993; Martens, 1971; Menon et al., 1993; Plank and Martents, 1974).

5. Mercury emissions through coal combustion and coal utilization by-products

5.1. Pathways of mercury emission

Coal contains significant quantities of many trace elements which are often, like Hg, bound in pyrite and sulfide minerals in coal. During combustion, the Hg in the coal is transformed into three species: (i) particle-bound mercury (Hg-p); (ii) vapor-phase elemental mercury (Hg^0), and (iii) vapor-phase oxidized mercury (Hg^{2+}), primarily as $HgCl_2$. Mercury in coal begins to volatilize at temperatures below 200 °C almost regardless of the mode of occurrence of Hg in the coal. At temperatures above 600–700 °C, Hg^0 is the only stable form (Galbreath and Zygarlicke, 2000; Zevenhoven and Kilpinen, 2001). At lower temperatures (350–400 °C) in the flue gas duct, with the presence of chlorine, sulfur and calcium, part of the Hg^0 vapor is oxidized into Hg^{2+}, and/or reacts with carbonaceous ash particles and is deposited as Hg-p. Hence, FA particle surface provides an important site for Hg absorption, especially when the Hg-p is oxidized. Brown (1997), and Rosenhoover (1999) observed that some coal FAs have properties (primarily carbon content and absorbed chlorine or sulfur) that promote Hg oxidation and/or Hg ash sorption. Many researchers (Carey et al., 1998; Hall et al., 1995) have concluded that FA can be a better medium for

separation of Hg from the flue gas stream than various special sorbents and activated carbon. However, the efficiency of Hg removal from flue gas by FA in relation to FA properties and other process parameters are not fully investigated (Hassett and Eylands, 1999; Sakulpitakphon et al., 2000).

For optimal removal of Hg from flue gas a high level of oxidation is beneficial since, contrary to Hg^0, $HgCl_2$ is water soluble which makes removal in wet flue gas desulfurisation units (FGD) possible. Particle-bound Hg-p facilitates its removal in dust control equipment such as baghouse filters and electrostatic precipitators (ESPs). For systems with selective catalytic reduction (SCR) of nitrogen oxides, increased oxidation of Hg is enhanced for bituminous coals but less effective for other coal grades (Brown et al., 1999; Meij et al., 2002; Srivastava et al., 2006; Zevenhoven and Kilpinen, 2001). Thus, coal-Hg is distributed in flue-gas clean-up residues, e.g. primarily in FAs and FGD residues. Association of Hg in bottom ashes is negligible, although a significant amount of Hg may be found in bottom ashes generated from coals with high content of pyrite (Senior et al., 2000). Mass distribution of Hg across different coal utilization by-products has been reported by Lee et al. (2006b) and Lee et al. (2006a) (see Fig. 6). This study revealed that over 60% of Hg from coal burning is associated with FA. Other studies have reported emissions of 90% or more of the coal Hg in flue gases to the atmosphere (Offen et al., 2005; Pavlish et al., 2003; Srivastava et al., 2006).

Meij et al. (2002) reported typical concentrations of 0.12 and 0.17 mg Hg/kg (dry) for typical steam coal fired in the Netherlands. This range of Hg concentration is similar to the coal from the Eastern United States. For FAs from five coal blends fired in the Netherlands an average Hg concentration of 0.28 mg Hg/kg (dry) was found during a seven-week testing, while the levels of Hg in wet FGD (gypsum) residues were in the range 0.06–0.92 mg/kg. Noting that electrostatic precipitators (ESPs) are operated at relatively low temperatures in the Netherlands, the coal Hg is partitioned as: ~25% emitted to the atmosphere and; ~50% is trapped in FA and ~25% is trapped in the FGD plant (~2/3 of this in ends up in FGD gypsum, ~1/3 ends up in waste water treatment plant sludge).

In the earlier EU-15 countries (mostly using imported coal blends similar to those used in the Netherlands) a total of ~56 Mt of CUBs was generated during the 1990s (Mukherjee et al., 2004). Combining this with the numbers given above (0.28 mg Hg/kg) for the Netherlands, corresponds to 10.2 t Hg in fly ashes, and 5.6 t Hg in FGD residues to be processed. For the same region Vom Berg et al. (2001), and Mukherjee et al. (2004) reported the following breakdown of coal by-product utilization in the year 1999: 56% (9.2 t Hg) in construction industry and civil engineering; 33% (5.5 t Hg) in restoration and into mines or pits; and 11% (1.8 t Hg) other uses. After the recent expansion of the EU with several large coal producers and consumers (e.g. Poland and Czech Republic) the current production of Hg from coal burning in the EU-27 might be several times larger than the above values.

In the US, regulations for Hg emissions from power plants (estimated at ~50 t/year) at the end of the 1990s, about 1/3 of total anthropogenic Hg emissions in the US are being implemented under the Clean Air Mercury

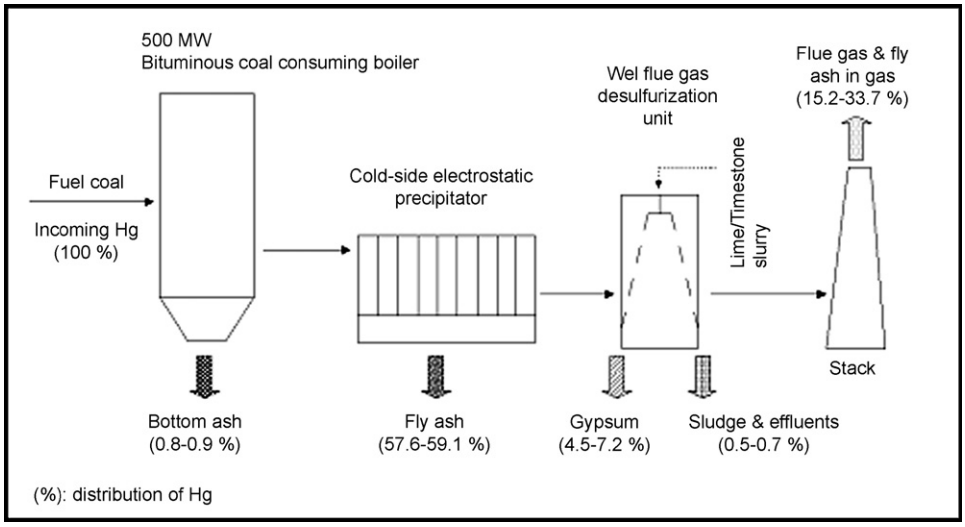


Fig. 6. Mercury balance in coal-fired power plant (modified from Lee et al., 2006b).

Rule (CAMR) (Sanford, 2005; Srivastava et al., 2006).[3] While increased amounts of Hg will be trapped by flue gas clean-up devices as these are optimized for higher Hg capture efficiency, it is likely that this will result in large amounts of spent sorbent solids that must be disposed. At sites where activated carbon (AC) sorbents will be used (providing Hg removal rates of 60–90%) the amounts of spent sorbent generated may be as high as 10 kg per g Hg absorbed. However, this amount can be decreased with significant progress in sorbent chemistry and optimisation of adsorption reactions involving the halogenated AC sorbents (Brown et al., 1999; Offen et al., 2005; Srivastava et al., 2006).

5.2. Mercury cycling

Trapping increased amounts of Hg in flue gas clean-up devices at power plants logically results in increasing amounts of Hg in CUBs. Several recent studies have identified temperature, humidity, solar radiation and the presence of water as important factors for the release of Hg from FA, FGD solids or mixture of both. From these studies it can be concluded that the release of Hg from CUBs into water or air at ambient conditions is insignificant (annual Hg releases of ~0.1% for a worst case scenario) with small effects of microbiological activity, and poses no risk to drinking water or air quality. In fact, most FA (with the exception of lignite-FA) actually absorbs Hg from the surroundings, acting as a sink. Interestingly, while FA and FGD materials show low Hg emission rates, mixtures of FA with FGD material and pyrite showed higher emissions, however still lower or comparable to natural emissions from local soils (Gustin and Ladwig, 2004; Heebink and Hassett, 2002; Xin et al., 2006). Release of Hg from FGD gypsum product used for wallboard is of great concern. The calcination of the gypsum at temperatures around 150–200 °C can result in Hg release of Hg up to 25%. At room temperature, however, there is little risk for Hg release from FGD wallboard since most Hg is present in the material in oxidized form, primarily as $HgCl_2$ (Heebink and Hassett, 2005).

Mercury-containing by-products are concentrated during pre-combustion coal cleaning for removal of pyrite sulfur and ash. This process also gives out significant levels of Hg (see e.g. Pavlish et al., 2003). Physical cleaning is common and effective when Hg is associated with coal in an inorganic form (Finkelman et al., 1979; Luttrell et al., 2000; Norton and Markuszewski, 1989). The removal efficiency by this process is quite wide, e.g. 0–26% for bituminous coal in the United States (Neme, 1991). Advanced cleaning technologies such as froth flotation, selective agglomeration, advanced cyclone design and several others have been reported. Conventional cleaning followed by selective agglomeration process claims reduction of Hg from coal ranging from 63 to 82% (average 68%) (Ferris et al., 1992; Pavlish et al., 2003).

6. Mercury flows via export and import of coal and coal fly ash

Studies on material and energy flows have been produced by the USGS and many other organizations such as Wupper Institute in the European Union (ETC/RWM, 2005; Loebenstein, 1994; Mukherjee et al., 2004; Sznopek and Goonam, 2000). "Whole material flow" concepts generally mean ecosystem management. The integrated approach between energy, biological, social or geological sciences help management and decision-makers to understand the problems of Hg in coal and coal-FA. When coal is transported over sea or land, local geography may assist the ecosystem management process significantly (Brown et al., 2000). Methyl mercury (Me-Hg) occurs only in areas where microorganisms or plant communities react with elemental Hg. It is necessary to understand the biogeochemical processes that contribute to entry of Me-Hg in food chain. In addition, we can mention here material flow cycles such as for Ag, Pb, Hg, and As in the United States where flow patterns have changed constantly due to modernization of policy and economic development. For example, due to restriction of Pb use in petrol, its flow in road/street has been minimized. Strict regulation policy and better controlled process technologies have minimized the emission of toxic metals in the environment of the western world.

After mining, coal is transported within the country where it was mined. Coal is exported and imported based on production and demand in a country. It is generally used in the energy sector as well as at home for cooking and heating purpose in the developing countries. Coal can contain exceptionally high concentrations of Hg with values as high as several ppm (Finkelman et al., 2002; Swaine, 1990, see Table 3).

During trading, it is necessary to know the concentration of Hg in the coal. In addition, the knowledge and

[3] The United Nations Environmental Program (UNEP) Governing Council met in Nairobi from 5 to 9 February 2007 and discussed Hg problems. The Governing Council adopted a decision that postpones for two years the question whether to initiate negotiations on a new legally binding global agreement.

fate of Hg in the combustion chamber or in the gas cleaning equipments, as well as partition of Hg in flue gases are crucial for power plant engineers. It has been used an averaged Hg concentration of 0.3 mg/kg coal as basis to calculate the amount of Hg formed in coal-fired power plants (Llorens et al., 2000; Weiss, 2005). The estimated annual discharge of Hg from coal for power generation from different countries are shown in Table 6.

Kobayashi (2004) estimated global export and import of coal for 2002 at 497 Mt (which implies that only 9.72% of total amounts produced crosses national borders) with a Hg flow of 149.07 t, assuming an average 0.3 mg Hg/kg coal (Fig. 7). This value will increase with the increased coal trade between countries and hence, it is necessary for the exporting and importing nations to know the quality of coal, e.g. Hg and other trace element concentration, as well as the contents of ash, sulfur and moisture content.

At the moment, there are no reports on export and import of coal-FA for countries or regions with in the EU. But Poland exports coal FA to the neighboring countries. It is generally processed and used inside a country where it is produced. In this review, it was estimated that the total production of coal-FA was at 413.7 Mt in year 2003 of which 393 Mt were recovered in flue gas clean-up systems, the rest being emitted into the atmosphere.

Table 6
Mercury concentration of world coal consumption, 2003

Country	Coal consumption (Mt)[a]	Hg in coal in metric tonnes[b]
Australia	129.73	38.92
China	1560.36	468.11
Germany	251.29	75.39
Greece	70.76	21.22
India	407.33	122.20
Japan	167.83	50.35
North Korea	29.94	8.98
Poland	140.61	42.18
Russia	220.45	66.14
South Africa	169.64	50.89
Turkey	64.41	19.32
Ukraine	68.04	20.41
USA	996.45	298.94
Others	835.38	250.61
Total	5112	1533.66

URL: http://www.eia.doe.gov/emeu/aer/txt/ptb1115.html.
[a] Mt, Million metric tonnes.
[b] We have assumed that world coal contains 0.3 mg Hg/kg coal. The same type of data has also been mentioned by Swaine (1990).

Considering global emission data of Hg from coal-fired power plant given by Pacyna et al. (2006) we find that our Hg concentration value in coal is of similar order of magnitude.

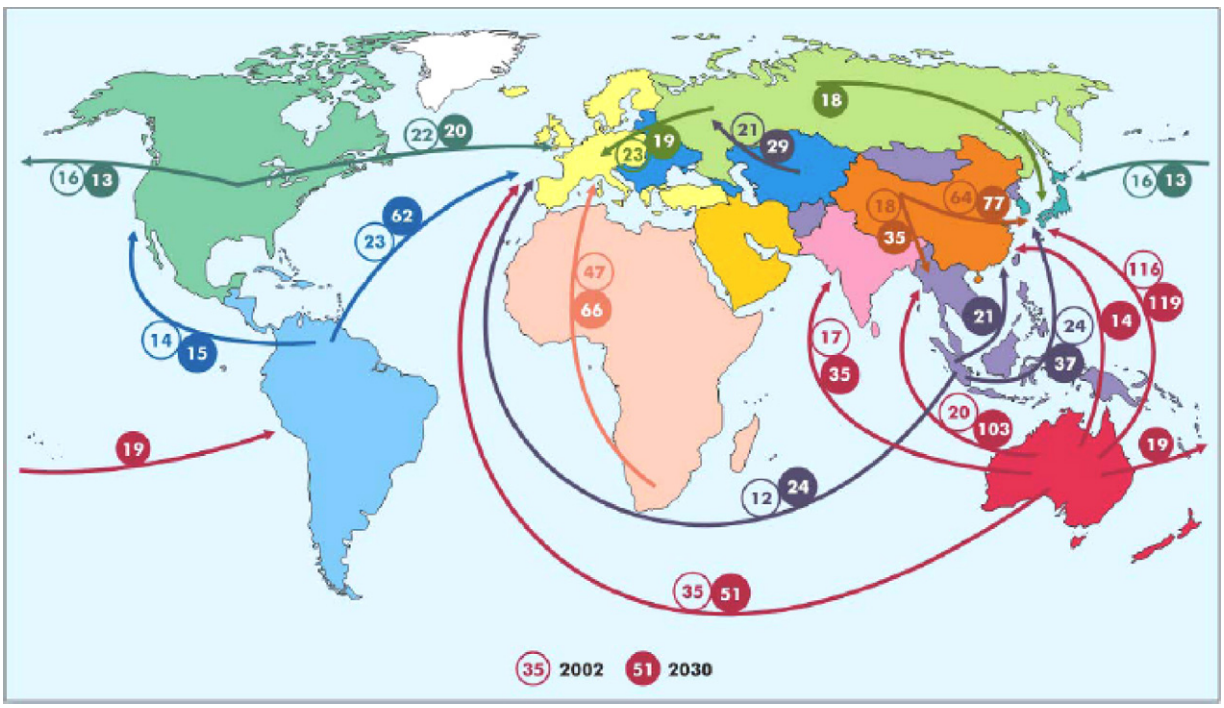


Fig. 7. Global coal flows. Hidden Hg flows can be calculated by multiplying with concentration value of Hg in coal. The ring without any color indicates the flow of Hg in 2003 (reproduced from Kobayashi, 2004).

7. Case studies

7.1. China

The recent economic development of China is due to rapid industrial growth that has resulted in deleterious affects on the environment in the urban and rural areas. In 2003, the total power generation capacity has reached 391 GW of which coal shared about 70%.

In 2003, China exported 82 Mt of coal with mean Hg concentration at 0.15 mg/kg (Belkin et al., 2006) which is equivalent to 12.3 t in 2003. Maximum Hg concentration was observed in coal samples of Guizhou Province is at 0.52 mg/kg (Streets et al., 2005), while in another study Belkin et al. (2006) estimated the concentration of Hg in Chinese coals by cold vapor atomic absorption spectroscopy, and reported Hg concentration in the range of 0.02–0.69 mg/kg (mean 0.15 mg/kg) based on 305 samples.

In China, major coal production occurs in its northern regions, particularly in the provinces of Hebei, Shaanxi and Inner Mongolia (IEA, 2004). Inside the country, coal is transported by railway wagons, truck and ship. It is believed that during transportation, a small part of the particulate and gaseous Hg from coal will pass into the atmosphere.

Atmospheric emissions of Hg in China have been studied by many researchers (Pacyna and Pacyna, 2002; Pacyna et al., 2006; Zhang and Wong, 2007). Streets et al. (2005) estimated that 38% of total Hg emissions in China originated from coal combustion where removal efficiency of the electrostatic precipitator (ESP) varied between 25.7 and 30.3% (Wang et al., 2000; Zhu et al., 2002). But in new large coal-fired boilers in China, the modern ESP has been erected for flue gas cleanup which will produce better quality FA (J. Lagon, *vide* Barnes and Sear, 2004).

In China, the residential sector utilized 123 Mt of coal (7% raw coal; 5% cleaned coal; 88% briquettes), in 1999, with no technologies to control particulate matter (PM) emissions. Health problems due to residential coal use have been recognized in different parts of China (Finkelman et al., 2002).

High Hg concentration in the atmosphere near the coal power plants and Zn-smelters in Guiyang City, Guizhou Province has exposed people to higher level of Hg through inhalation, which may affect health problems in the regional level, where as in southern China, long-term exposure of Hg through consumption of fish has caused increased level of skin disorders and even disorder of brain development (autism) among the children (Ko, 2004; Zhang and Wong, 2007).

Bioaccumulation and biomagnification of Hg may cause concern on food safety and human health. In many areas of China enhanced scavenging of Hg as water-soluble Hg^{2+} as well as particulate Hg occurs due to high humidity, acid rain and heavy rain fall. Therefore, Hg from the atmosphere will contaminate soils, water and sediments (Kabata-Pendias and Mukherje, 2007; Sakata and Marumoto, 2005) polluting the region, endangering human life and aquatic species. An increasing demand of coal has been projected in China at an average rate of 2.2% and the thermal power sector will utilize 73% of total Chinese coal in 2030 (Koukouzas et al., 2006).

7.1.1. Coal fly ash production and uses in China

Between 1949 and 2000, 2.2 billion tonnes of coal-FA have covered 300 square kilometer of useful land in China (Barnes and Sear, 2004). Due to industrialization, it is reported that the FA production in China is about 160 Mt per year (Koukouzas et al., 2006; Ye, 2001). Atmospheric emissions of FA in China have not been documented in the literature, but it can be predicted that approximately 10 Mt of FA is released annually across the country. It is also important to note that between 35 and 40% of FA is disposed into ponds and piled on land (Barnes and Sear, 2004).

There is nowadays encouragement from the Chinese government to use coal-FA in different sectors. It has been reported that about 70 Mt of FA (F type according ASTM C618) is used as building materials, road construction, cement industry and agricultural land applications (Cheng et al., 2004). The utilization pattern will increase slowly but surely and become more diverse in the future. Chinese coal ash can be divided into high and low calcium. There is better market when FA contains low carbon (>5.0%) and finer the ash particles. There is general consensus leading towards decreased environmental pollution by increased utilization of the FA. In 2005, China utilized about 65% of coal FA due to new construction regulation (Barnes and Sear, 2004).

7.2. India

Coal is a dominant commercial fuel in India and 565 mines are operated by Coal India and other subsidiaries. In 2003, production of hard coal was 358.4 Mt while utilization was 407.33 Mt. India is the sixth largest electricity generating and consuming country in the world. Mukherjee and Zevenhoven (2006) recently discussed Hg in coal and coal-FA in the Indian subcontinent. There is a time delay in data for trace elements in Indian coal and coal combustion by-products from the United States Geological Survey. Recently, Tewalt et al. (2005)

have collected 108 coal samples from India to have quality information of coal that will play an important role in national and international environment, economy and energy policy in the country. Mukherjee and Zevenhoven (2006) reported an apparent lack of information on Hg in Indian coals and coal-FA. Based on the report summarized by Rajagopalan (2003), Mukherjee and Zevenhoven (2006) estimated coal-FA in India may contain around 0.53 mg Hg/kg with a total Hg content estimated at 41.16 t.

7.2.1. Use pattern of coal fly ash in India

Fly ash can be considered as the world's fifth largest raw material resource. An estimated 25% of FA in India is used for cement production, construction of road and brick manufacture (Bhattacharjee and Kandpal, 2002). The FA utilization for these purposes is expected to increase to nearly 32 Mt by 2009–2010. Currently, the energy sector in India generates over 130 Mt of FA annually (Burke, 2007) and this amount will increase as annual coal consumption increases by 2.2%.

The large-scale storage of wet FA in ponds takes up much valuable agricultural land approximately 113 million m^2 and may result in severe environmental degradation in the near future that would be disastrous for India. Recently an organization has been established to address the following issues (Kumar et al., 2005): (i) FA characterization; (ii) hydraulic structure; (iii) handling and transport; (iv) ash pond and dams; (v) agriculture related studies and applications; (vi) reclamation of ash ponds for human settlement; (vii) research and development; (viii) building materials.

7.2.2. Material flow

There is limited information on material flow programs in India. In the west, material flow programs support sustainable use of resources by building a strong foundation, expanding the range and number of customers and creating partnerships. Material flow analyses should be integral part of any "material flow program". When coal is transported from the eastern to southern regions of India both suppliers and receivers are expected to produce and use correct analyses data which will help to establish the quality of coal and its price. The cost of environmental restoration must be estimated for a prior assessment of the economic impact of using FA containing high levels of Hg (or arsenic) during the manufacture of building materials.

It is quite understandable that the energy sector plays a crucial role for India's industrial growth, job opportunities in rural and urban regions, and to fulfill the basic human needs. Hence state-of-the-art technology in the energy sector is necessary to meet the socio-economic goals enhancing electricity production capacity and consumption. The new technology must be high efficiency combined with better pollution control for particulates, NO_x, SO_2 and also CO_2. Any technology introduced in India or China should be cost-effective and suitable for the coal available in the country. Many advanced technologies are available in the power generation sector. For example, circulating fluidized-bed boilers have been introduced in the West to utilize lower quality coals, biomass and waste materials. Oxygen may replace firing in air for easier carbon capture. Also coal gasification-based systems may be introduced in these countries (Chikkatur and Sagar, 2005). For India, monitoring and feasibility studies are vital for the selection of proper technologies in the future.

7.3. Australia

Australia relies on coal to produce over three-quarters of its electricity (76.9%). Mercury concentration in coal and FA has been cited in Table 3. At present about 13 Mt of coal combustion products are annually produced of which 70% is used in landfills (Yunusa et al., 2006). The long-term use of FA in landfills has documented health hazards and environmental problems.

The thrust of contemporary research is on the safe use of FA containing hazardous and non-hazardous trace elements in agricultural soils. In Australia, dry salinity has affected 5.7 M hectares of land which could expand to 17 M ha by 2050 (National Land and Water Resources Audit, 2005). Yunusa et al. (2006) studied particles in fly ashes which fall between the fine and slit categories. Its pore structure alters soil properties (e.g. bulk density, porosity, hydraulic conductivity, and water retention) that are positive for plant growth (Jabro, 1992). Many trace elements in FA are considered to be either of major concern (such as As, B, Cd, Hg, Mo, Pb, Se) or moderate concern (e.g. Cr, Cu, Ni, V, Zn and F) based on the risk of their release into the environment. Above mentioned elements occur at quite low concentrations in Australian FA (Yunusa et al., 2006). Studies by Killingley et al. (2000) revealed considerable variations in the trace element concentrations in FA in acidic and alkaline ashes. In acidic ash, Hg concentration varies between 0.01 and 0.08 mg/kg whereas in alkaline ash, it is between 0.07 and 0.23 mg/kg. These values are still lower than in fertilizers (5.0 mg Hg/kg) used in Australia. Australian limits are still provincial and also depend on fertilizer type (Australian Soil Fertility Manual, 2006). It is believed that the risks in using Australian FA in soil management are very limited, although Heidrich (2003) pointed out

Table 7
Fly ash production in EU-10 new member states (reproduced from Barnes and Sear, 2004)

Country	Production in 2000 (Mt)	Comments
Bulgaria	5.6	
Czech Republic	10.4	Including brown coal ash
Estonia	5.0	Oil shale ash
Hungary	3.4	
Latvia	23.2	Tones
Lithuania	–	Not known
Poland	10.3	
Romania	6.4	
Slovak Republic	1.3	
Slovenia	1.3	Data for 2002
Total	44	

an absence of and conflicts in the various existing of state and commonwealth regulations on utilization and guidelines of FA for land management. However, FA could effectively improve soil pH, but there is no evidence that FA improve other physical soil properties. Fly ash is very effective, however, in the case of very acid soils (Alina Kabata-Pendias, personal communication, 28 May 2007).

7.4. New EU-27 countries in Eastern Europe

Among the new EU-27 member states, Poland, the Czech Republic and some extent also Hungary produce and consume considerable quantities of hard coal and/lignite. Poland followed by the Czech Republic produce hard coal annually at 145 and 73 Mt, respectively. The details on FA production from these new EU-10 member states is shown in Table 7. The Czech Republic and Poland produced about 10.4 and 10.3 Mt for 2000, respectively. Fly ash utilization has a long history in Poland. In 1972, Poland has utilized 32% of FA generated from power stations that has increased to 70% in the year 2001.The FA is also traded between Poland and other EU neighboring countries (Barnes and Sear, 2004).

7.5. Korea and Japan

Mercury emissions for East Asia have increased over the past several decades, but anticipated growth is currently being moderated in part by improved coal preparation and combustion technologies (Carmichael et al., 2002).

In Korea, there has been dramatic reductions in total amount of anthracite consumption (heating fuel for residential facilities) between the late 1980s (2.5 Mt/y) and late 1990s (0.3 Mt/y) (Kim and Kim, 2000). However, bituminous coal use in power plants has exhibited a continuous increase since the late 1970s: 0.2 Mt/y in 1979 and 50 Mt/y in 1999 (Kim and Kim, 2000). As the consumption of anthracite has decreased considerably, it is possible to say that the use of bituminous exerts significant influence on Hg emissions (Kim and Kim, 2000). Approximately 3.7 Mt of FA were produced in 1997, and its production will reach at 6.0 Mt by 2010 (Cha et al., 1999). The use of FA in cement industry is beginning, but a large portion of FA will require for other environmentally friendly uses (Lee et al., 2006a).

In Japan, most coal-fired power plants have already installed devices to control emmission (Ando, 1990). The mean Hg concentration in coal is at 0.05 mg/kg while the Hg emission rate is 4.4 μg/kWh; the total annual Hg emission in Japan from coal-fired power plants is estimated to be 0.6 t/y (Ito et al., 2006). It is reported that the adverse effect of the Hg emissions from the coal-fired power station is quite small because maximum annual mean ground level Hg concentrations are in the order of 10^{-2} to 10^{-5} of the background concentrations (Ito et al., 2006). The coal ash generation was about 8.8 Mt in 2001, and its ratio of fly ash to bottom ash is 90:10 (NEDO, 2006). About 80% of the generated ash is used in various sectors—cement (75%), civil engineering (13%), construction (5%), agriculture (2%) and others (5%) (NEDO, 2006).

7.6. Russian Federation

Russia has one of the world's largest coal reserves containing 375 billion tonnes. Of this total, more than 250 billion tonnes are recoverable reserves and 140 billion tonnes consist of lignite coal. The production of hard coal for Kazakhstan and Ukraine (Russia) for the year 2004 is shown in Fig. 1 and total consumption was cited in Table 5. The present coal-fired power plants in Russia and Kazakhstan are very old and these plants will reach the end of their economic life within the next 20 years (Barnes and Sear, 2004).

Mercury in Russian coal is reported at 0.02–0.9 mg/kg whereas Yudovich and Ketris (2005a) mentioned a Hg content in Siberian bituminous coal of 0.02–0.04 mg/kg. In brown coal it varies between 0.03 and 0.05 mg/kg. These authors also discussed the geochemistry of bituminous and brown coals where they mentioned the highest concentration of Hg (0.01–30 mg/kg, mean 1.21 mg Hg/kg) from the Central zone of Donbas region, Russia (Yudovich and Ketris, 2005b). Over 70% of this Hg enters into the atmosphere from heat and electricity generation (Yagolnitser et al. *vide* Yudovich and Ketris, 2005a).

It is reported that coal-fired power plants in Russia produced more than 75 Mt of FA and sinter waste in 2000. About 11% of the product was re-used for production of secondary construction materials. There are only few marketing opportunities for FA because power plants are situated close to coal fields and far from potential FA users. Fly ash is often transported by boat using rivers and lakes. Besides this, there is considerable concern for environmental impact from historical ash deposits (Barnes and Sear, 2004).

7.7. South Africa

In South Africa coal production and consumption are shown in Fig. 1 and Table 6, respectively. The 93% electricity generation stem from coal which ranks it second in the world after Poland (94.8%). The quality of South African coal is quite poor due to its low calorific value and high percentage of ash (>33%). Annual production of FA is estimated to range between 22 and 24 Mt. Chemical composition of FA indicates that it contains trace elements such as Al, Zn, Pb, Cu, Sb, Hg, Ni, Y, V, Th, Ge, Ce and U. These elements are brought into the coal basin due to chemical weathering of the crustal rocks. In South African FA is pumped as slurry to ash-heaps after carbon extraction, and ash heaps are quite hard. This limits the use of this material in the country (Petrik et al., 2003).

Based on a detailed research, the principal application of FA for cement industries is recommended due to the key properties such as: (a) spherical nature of the particles; (b) a highly reactive aluminosilicate pozzolan; (c) low content of alkali elements; (d) low carbon content (<5%). These properties suggest that less water is needed for the production of concrete. Moreover, FA is used within other different sectors in South Africa, such as in polymer industry, rubber industry, agriculture and many others (Krueger and Krueger, 2005).

7.8. South America

World Coal Quality Inventory (WoCQI) made by the United States Geological Survey (USGS) for a short period time (1998–2005), addressed the status of coal in nine countries of South America including Argentina, Brazil, Colombia, Peru, Venezuela, Bolivia, Ecuador, Paraguay and Uruguay (Karlsen et al., 2006), focusing on quality, resource availability, export opportunities, technologies, by-product and disposal issues. Production, consumption and export data are summarized in Table 8. Available data of Hg for five countries are cited in Table 3. The sub-continent relies more on hydroelectric power than on coal for its power generation. Brief scenarios of coal in these countries are mentioned below.

Argentina steadily ceased coal production in 2003. There are 27 power plants of which 26 facilities depend on oil and gas. But metal industry depends on metallurgical coal which is partly imported 420 kt yearly from New South Wales, Australia (Mineral Resources of New South Wales, 2001) and 70 Mt of coal yearly is transported by ship to Buenos Aires for metallurgical purposes.

Recoverable coal in Brazil is found in the Rio Formation of the Paraná Basin, which is located in the southernmost region of Brazil (Weaver, 1993). Brazilian coal contains high ash (20.5–64.2 wt.%) and the sulfur contain varies between 0.3 and 11.5 wt.%. Mercury concentration in washed coal was estimated to be about 1 mg/kg. The country produces 4.2 Mt coal per year which is not enough for the country and 15 Mt of coal was

Table 8
South American coal production, consumption, import, and export (unit: Mt/y)

Country	Production	Consumption	Import	Export	Year	Reference
Argentina	0.057	–	0.825	–	2002	Karlsen et al. (2006)
Brazil	4.2	20.1	15.9	–	2002	Energy Information Administration (2004)
Chile	0.5[a]	4.63	–	–	2000	Karlsen et al. (2006)
Colombia	49.3	3.86	–	45.3	2003	Karlsen et al. (2006)
Peru	0.062[b]	–	–	–	2000	Karlsen et al. (2006)
Venezuela	7.69	–	–	–	2001	Karlsen et al. (2006)
Bolivia	–	–	–	–		Karlsen et al. (2006)
Ecuador	–	–	–	–		Karlsen et al. (2006)
Paraguay	–	–	–	–		Karlsen et al. (2006)
Uruguay	–	–	–	–		Karlsen et al. (2006)

(–) Not known.
[a] Year 2003.
[b] Bituminous coal: 45,000 t.

imported in 2002 (Energy Information Administration, 2004). However, Brazil has the second largest coal reserve in the South America. Domestic production is used for power generation and the imported quantity is used for the iron and steel industry.

Colombia has coal reserves of 6.8 billion metric tonnes of which 94% is anthracite and bituminous coal (Energy Information Administration, 2003). Production, consumption and export of coal are presented in Table 8. Although coal does not play a significant role for the national development, the country has exported 6.9 Mt steam coal to the United States. In 2003, 45.3 Mt of coal was exported containing 0.02–0.17 mg Hg/kg, which accounts for about 0.9–7.7 t of Hg were transferred during trading of coal.

Venezuela is the second country after Colombia in South America in terms of coal resources (Fossil Energy International, 2002). The country has 10 billion metric tons of coal deposit. Its export capacity has recently increased by 400%. Coal production is quite limited due to poor infrastructure, but the country has plans to increase coal production by 20 Mt in the year 2008 (Energy Information Administration, 2002). The country exported 6.4 Mt of coal to the EU countries and its Hg concentration is mentioned in Table 3. The 75% of the exported products are used in the energy sectors and the rest (25%) in the metallurgical plants.

Peru is not a coal producing country, and there is lack of information about Peruvian coals. Baruya and Clarke (1996) estimated recoverable Peruvian coal to be around 11 Mt which ranked 39th worldwide. Due to high sulfur content, coal is imported from Indonesia, Colombia and Venezuela for copper mining and smelting. It is also used in rural areas for cooking, brick making, metallurgical industry, and cement production (Mucho, 1992). Analysis of a limited number of Peruvian coal samples ($n = 16$), indicated Hg concentration at 0.63 mg/kg (Brooks et al., 2001) which is quite high.

Other countries of South America such as Bolivia, Ecuador, Paraguay and Uruguay do not depend on coal due to the lack of adequate coal resources of economic importance (Alvardo, 1980; Baruya and Clarke, 1996). However, these countries import small quantity of coal for industrial application.

8. Conclusions

Increased utilization of coal for power generation results in the production of large amounts of CUBs such as FA and flue gas desulfurisation (FGD) gypsum. Export of coal from a country where it was mined, to another country results in relocation of the Hg that was present in the coal. The presence of Hg in CUBs material must be considered. In this paper the amounts and concentrations of Hg in hard coals and CUBs from different sources of coals are summarized. Due to physiochemical properties of Hg, it will cross the boarder of a country through atmosphere, rivers and seas, causing environmental problems and health effects of humans. Many countries including India and China do not have commitments under the 1997 Kyoto Protocol framework, but the decision-makers should understand that clean air is necessary for health and quality of life. In all big cities, air pollution gives health problems causing respiratory infections, lung disease and cancer. The socio-economic costs of health problems caused by air pollution might be billion dollars for a country like India or China.

Hence, it is necessary to understand the material flows and the technical, environmental and economic advantages related to coal and the CUBs such as the FA and their importance to the society. Besides, it is also important to study and assess the flow of Hg in coal and the CUBs and their effects on the atmosphere, soils and aquatic environment. During export and import of coal, it is also necessary to address the concentration of Hg in coals so that suppliers and buyers realize the fate of Hg in the high temperature process.

In addition, we would like to add that technological collaboration is indispensable to reduce Hg and other trace elements problems in the society and their flows from energy sectors where fossil fuels, primarily coals, are used. When emissions are reduced, enhanced Hg flows through raw materials and trading of Hg in coal will be minimal. But the international society must exchange knowledge, resources and harmonize standards. Policy makers should also allocate funding on renewable energy technologies which will slow down source depletion, and diminish environmental pollution such as Hg and its flow through coal and the coal utilization by-products. Besides, campaign should be launched addressing the potential users regarding benefits of the uses of FA and the material should be readily available and cost-effective.

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