Technologies and practices on atmospheric mercury emission control

(Draft)

Contents

1 Coal-fired power plants and industrial boilers

Boilers are facilities designed to burn fuel to heat water or to produce steam. The steam produced from the boiler can be used for electricity production or used in industrial processes; likewise hot water can be used in industrial processing, or for domestic and industrial heating. Although mercury content of coal is low, the total atmospheric mercury emission from coal-fired power plants and industrial boilers could be large due to the large amount of coal burning.

1.1 Boiler types

1.1.1 Utility boilers

Utility boilers are very large in comparison to modern industrial boilers. A typical large utility boiler produces in the order of 1,600 tons of steam per hour.

Utility boilers are usually designated by the combustion furnace configuration:

- Tangentially fired: Commonly used for pulverized coal combustion but may be used for oil or gas; single flame zone with air-fuel mixture projected from the four corners of the furnace tangential to furnace centre line;

- Wall fired: Multiple burners located on a single wall or on opposing furnace walls can burn pulverized coal, oil or natural gas;

- Cyclone fired: Typically crushed coal combustion, where the air-fuel mixture is burnt in horizontal cylinders;

- Stoker fired: Older plants burning all solid fuel types; spreader stokers feed solid fuel onto a combustion grate and remove ash residue;

- Fluidized bed combustion: Lower furnace combustion temperature, efficient combustion promoted by turbulent mixing in the combustion zone, crushed coal feed with the potential for sorbent additions to remove pollutants, particularly sulphur dioxide;

- Pressurized fluid bed combustion: Similar to fluidized bed combustion, but at pressures greater than atmospheric, and with higher efficiency.

1.1.2 Industrial boilers

Industrial boilers are normally identified by the methods of heat transfer and combustion system utilized. In summary, the heat transfer systems are:

- Water tube boilers: Heat transfer tubes containing water are directly contacted by hot combustion gases. Commonly used in coal-fired installations but can accommodate almost any combustible fuel including oil, gas, biomass, municipal solid waste and tyre-derived fuel;

- Fire tube boilers: Water surrounds tubes through which hot combustion gases are circulated. The application is more common for pulverized coal, gas and oil-fired boilers, but various types can also burn biomass and other fuels. Generally used for lower-pressure applications;

- Cast-iron boilers: Cast sections of the boiler contain passages for both water and combustion gas. Used for low-pressure steam and hot water production, generally oil or gas fired with a smaller number of coal-fired units.

And the combustion systems are mainly:

- Stokers: There are a variety of different stoker types and functions. Underfeed stokers supply both fuel and combustion air from below the grate, discharging ash to the side or rear. Overfeed stokers, which may be mass feed or the more popular spreader stoker, supply the combustion air from below the grate, with the fuel for combustion being distributed above the grate. Spreader stokers with a stationary grate are used extensively in the sugar industry to combust bagasse;

- Burners: This diverse group of devices manages the delivery of air-fuel mixtures into the furnace under conditions of velocity, turbulence and concentration appropriate to maintain both ignition and combustion.

1.2 Mercury emission from coal combustion

Coal contains trace amounts of mercury. Mercury content of coal varies largely among different coal producing areas, usually in the range of 0.01-0.3 mg/kg. Because the combustion temperature of coal in boiler is above 1000°C, more than 99% of the mercury releases into the flue gas during coal combustion in the form of elemental mercury (Hg^0). With flue gas temperature decreasing from the core burning area to the flue gas outlet of the boiler, Hg^0 reacts with other components in the flue gas (fly ash)

and partially converted to gaseous oxidized mercury (Hg^{2+}). Part of the gaseous mercury adsorbs onto the surface of fly ash and forms particulate-bound mercury (Hg_p). The mercury transformation process during coal combustion is shown in Figure 1-1.
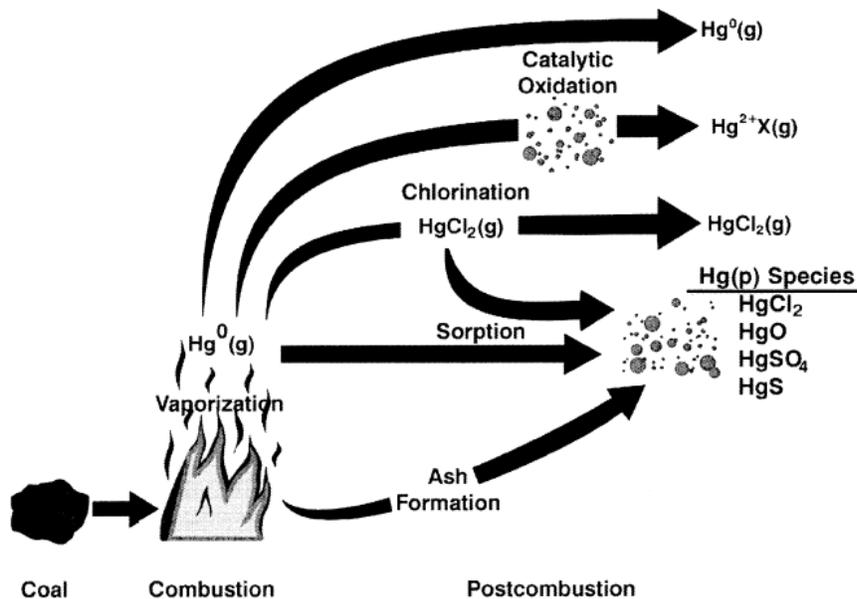
Figure 1-1   Mercury transformation on coal combustion

Hg^{2+} includes $HgCl_2$, HgO, $HgSO_4$, etc. Hg_p exists in elemental or oxidized form. Post-combustion NO_x control measures can also cause mercury oxidation. The degree of mercury oxidation and the mercury species generated have impacts on the synergistic mercury removal efficiency.

Compared with the measurements of SO_2, NO_x and PM emissions, that of mercury is more challenging and expensive due to the low concentration level of mercury in flue gas ($\mu g/m^3$ level). Although onsite measurements of mercury emission from a single boiler to the atmosphere are encouraged to improve understanding of atmospheric mercury emission, it is impossible to measure all the coal-fired facilities.

Another approach instead of direct measurement is to use the mercury content of coal, the amount of coal burned and the mercury removal efficiency of air pollution control devices (APCDs) to calculate the atmospheric emission of mercury. The commonly used equation is as follows:

$$E = \sum_i \sum_j \left[M_i \cdot A_{i,j} \cdot (1 - P \cdot w) \cdot R_j \cdot \left(1 - \sum_k C_{j,k} \cdot \eta_{j,k} \right) \right] \qquad (1\text{-}1)$$

where E is the total mercury emission; M is the mercury content of coal; A is the amount of coal consumption; P is the application rate of coal washing; w is the mercury removal efficiency of coal washing; R is the mercury releasing rate of boiler; C is the installation rate of a certain APCD; η is the mercury removal efficiency of a certain APCD; i is the province; j is the boiler type; k is the type of APCD.

1.3 Best environmental practices

The best environmental practices described in this section constitute general guidance applicable to any kind of boiler, regardless of its size or type:

- Identify key process parameters, either from site-specific investigations or research undertaken on similar facilities elsewhere;

- Introduce measures that enable control of key process parameters;

- Introduce monitoring and reporting protocols for key process parameters;

- Introduce and follow planning cycles, implement appropriate inspection and maintenance cycles;

- Introduce an environmental management system that clearly defines responsibilities at all levels;

- Ensure adequate resources are available to implement and continue best environmental practices;

- Introduce process improvements to reduce technical bottlenecks and delays;

- Ensure all staff are appropriately trained in the application of the best environmental practices relevant to their duties;

- Define a fuel specification for key fuel parameters and introduce a monitoring and reporting protocol;

- Ensure the environmentally sound management of fly ash, coarse ash and flue gas treatment residues;

- Ensure that, when co-firing biomass or waste, they should not be added until the boiler furnace combustion conditions are stable and it has reached its operating temperature.

1.4 Best available techniques

1.4.1 Adjustment of energy structure and improvement of plant efficiency

1.4.1.1 Adjustment of energy structure

Atmospheric mercury emission is not involved in the producing processes of wind power, solar power, hydro power and other renewable energy. Therefore, energy restructuring is an important way to reduce mercury emissions. Development of clean energy and control of the total coal consumption can reduce atmospheric mercury emissions from the origin.

In addition, the use of alternatives such as natural gas can also significantly reduce mercury emissions.

1.4.1.2 Improvement of plant efficiency

Improving various areas of operation within an older boiler can reduce mercury emissions. Many existing plants could be overhauled to improve both efficiency and output while reducing mercury emissions in an economic manner. Improvement of plant efficiency may involve a number of measures designed to conserve fuel (coal) and, as a result, to reduce the amount of mercury emissions. Some of the most commonly applicable measures are shown in Table 1-1 and include: new burners, improved air preheater, improved economizer, improved combustion measures, minimization of short cycling, minimization of gas-side heat transfer surface deposits, and minimization of air infiltration.

In addition, O&M practices have a significant impact on plant performance, including its efficiency, reliability, and operating cost. Good O&M practices can significantly slow down the deterioration rate of a power plant. Some of the good O&M practices include, for example, steam line maintenance and water treatment. A well operated and maintained plant will experience less rapid deterioration of heat rate; hence, O&M practices themselves influence coal use and mercury emissions. It is important to distinguish normal maintenance from capital expenditure. Capital expenditure is typically only done once every few years and includes repairs/replacement of major equipment all at one time. Good O&M practices should be an ongoing concern in daily plant operation.

Table 1-1   Commonly applicable efficiency improvement measures at power plants

Measure	Efficiency Improvement (% points)	Mercury Reduction Potential, (%)	Comments
Replace/Upgrade Burners	Up to 4-5%.	Up to ~ 6%.	Site-specific considerations (ability to retrofit)
Improved Economizer	40°F increase in flue gas temperature equals a ~1% efficiency loss	Relates to efficiency gain in boiler	
Improved Air Preheater	A 300°F decrease in gas temperature represents about 6% improvement	~ 1% per 40°F temperature decrease	
Combustion Tuning	CO from 1000-2000 to < 200 ppm UBC from 20-30% to 10-15%	up to ~3%	Manual tuning with parametric testing
Combustion Optimization	0.5 – 3.0	up to ~ 4%	Neural network-based
Instrumentation and Controls	0.5 – 3.0 (in addition to optimization)	up to ~ 4%	
Minimize short cycling	Up to ~ 4% – 6%	Up to ~ 5% -7%	Very site specific
Reduce slagging and fouling of heat transfer surfaces	1% to 3%	Up to ~ 4%	Site specific; fuel quality/operating condition have large impact
Reduce air leakages	1.5 – 3%	Up to ~ 4%	Requires routine maintenance procedures

1.4.2   Pre-combustion coal treatment

Coal treatment includes conventional coal washing, beneficiation, blending, and coal additives. Conventional coal washing, while primarily targeting the minimization of ash and sulfur content of coal, can also decrease the mercury content of coal. Coal beneficiation includes coal washing and additional treatment designed to decrease the mercury content of coal. The remaining coal treatment technologies (coal blending and coal additives) have been designed to specifically address minimization of mercury emissions by promoting chemical transformations of mercury in the power

plant's combustion and post-combustion equipment that facilitate mercury removal. They can be used in addition to coal washing (e.g., blending of two streams of washed coal) or as stand-alone approaches.

1.4.2.1 Coal washing

Conventional coal cleaning methods separate the organic fraction of the as-mined coal from the mineral materials according to the differences in either the density-based or surface-based characteristics of the different materials. Physical coal cleaning typically involves a series of process steps including size reduction and screening, gravity separation of coal from sulfur-bearing mineral impurities, and dewatering followed by drying. Conventional coal cleaning methods will also remove some of the mercury associated with the incombustible mineral materials. However, they will typically not remove the mercury associated with the organic carbon structure of the coal (EPA, 2001). The review quotes test data for 26 bituminous coal samples that indicate a wide range in the amount of mercury removed by coal cleaning. Analysis of five of the coal samples showed no mercury removal associated with conventional coal cleaning while the remaining 21 coal samples had mercury reductions ranging from approximately 3 to 64%. The average mercury reduction for all of the data was approximately 21%. Another study quoted by the review above reported higher average mercury reductions for 24 samples of bituminous coals. These data also showed a wide range in mercury reduction rates. The average decrease in mercury reduction on a mass basis was 30%.

The variation in mercury reductions quoted above might be a function of the type of process used to clean a given coal and the nature of mercury in the coal matrix. In addition to some elemental mercury and cinnabar, mercury may be present in coal bound with pyrite or with the organic fraction of coal (ACAP, 2004). The heavier pyrite can be removed by density-based processes, but not by surface-based processes where the similar surface characteristics of pyrite and the organic matter make separation of the two components difficult (EPA, 2001). Advanced coal cleaning techniques, such as the ones using naturally occurring microbes and mild chemical processing, were investigated in the past in order to augment mercury removal (Brown et al., 1999).

1.4.2.2 Coal beneficiation

Coal beneficiation is capable of improving coal properties beyond what can be

achieved with coal washing alone. It includes coal washing as a primary step, but then utilizes additional treatment to reduce the mercury content of coal. An example of coal beneficiation may be the K-Fuel process. The process may also be described as a pre-combustion multi-pollutant control process, as it results in reduction of mercury emissions in addition to lower PM, SO_2, and NO_X emissions. K-Fuel is a beneficiated coal that is derived from subbituminous coal or lignite coal (Black and Veatch, 2003). The resulting fuel is lower in ash, higher in heating value, and produces lower pollutant emissions than untreated coal. K-Fuel uses a pre-combustion process that improves the quality of the coal—including removing the mercury, moisture, ash, sulfur, and some of the fuel NO_X precursors—before the coal is burned at the power plant. Because these constituents are removed prior to burning the coal at the plant, the need for post-combustion controls may be reduced. K-Fuel technology may be applicable to bituminous coal as well. According to K-Fuel, physical separation studies on a number of low-rank coals exhibited 10 to 30% ash reduction, 10 to 36% sulfur reduction, and 28 to 66% mercury reduction. Thermal separation adds more mercury reduction. Testing by Rio Tinto Technical Services in Perth, Australia showed a 40% reduction in fuel mercury due to thermal separation alone. Total mercury reduction at pilot-plant facilities was reportedly 66 to 67% (Gunderson, 1993 and Vesperman, 1993). NO_X reductions of 40 to 46% have been experienced for K-Fuel (Alderman, 2003). Another demonstration completed in 2006 and using subbituminous coal for K-Fuel production revealed an SO_2 emission reduction of 38-40% and NO_X emission reduction of 10-22%. The K-fuel process delivered a mercury emission reduction of up to 70% (KFx, 2006).

1.4.2.3 Coal blending/switching

Coal blending/switching at power plant is quite commonly used as power plants attempt to cost-effectively meet SO_2 emission limits. For example, in the U.S. some plants blend low-sulfur Powder River Basin (PRB) subbituminous coal with bituminous coals (typically with high sulfur content) to reduce SO_2 emissions without FGD installation. As a side effect of this SO_2 emission control strategy, mercury speciation may be altered, thus compromising mercury capture in a downstream FGD (if one is available). Bituminous coals typically produce higher fraction of oxidized mercury in the flue gas than do subbituminous coal. Since oxidized mercury is water-soluble it is more readily captured in FGD systems. Consequently, the mercury capture efficiency of FGD systems depends largely on the fraction of oxidized

mercury at the FGD inlet (Miller et al., 2006). Coal blending has the potential of increasing the mercury capture by about 80%. A comprehensive study of the effects of coal blending on mercury speciation in the presence of SCR examined the oxidation of mercury using blends ranging from 10 to 40% subbituminous PRB with bituminous coal (Serre et al., 2008). The SCR inlet/outlet oxidized mercury concentration was higher for the 100% bituminous coal firing (27%/84%) than for the 100% subbituminous coal firing (6%/3%).

1.4.2.4   Coal additives

The amount of mercury oxidation increases with the amount of chlorine in coal. However, the concentration of chlorine in the coal often may not be sufficient to achieve a high level of mercury oxidation. To overcome this issue, approaches have been designed to add halogen compounds such as bromine or chlorine salts. Alternatively, hydrogen chloride (HCl) or ammonium chloride (NH$_4$Cl) may be added. Halogen additives oxidize elemental mercury and make it available for capture by downstream devices. They may be particularly useful in improving mercury removal for units firing low-chlorine subbituminous coals. The additives may be sprayed on coal, injected into the boiler, or added as solids upstream of the coal pulverizer. Full-scale tests were conducted using a KNX additive (52 wt % water solution of calcium bromide) as a pre-combustion additive at a 25 ppm in coal equivalent level. A mercury emission reduction of 92-97% was consistently observed on a 600 MW unit firing subbituminous coal and equipped with an SCR (Rini and Vosteen, 2009). Bromide salts can promote the oxidation of mercury even if only small amounts are added. This was confirmed in an extensive testing program by the Electric Power Research Institute (EPRI). Full-scale tests conducted at 14 units firing low Cl coals demonstrated more than 90% of flue gas mercury oxidation for bromide additions equivalent to 25 to 300 ppm in coal (Chang et al., 2008). The comparison of performance of bromine-based and chlorine-based additives is shown in Figure 1-2 and gives the percent oxidation of elemental mercury as a function of halogen addition rate (Vosteen and Lindau, 2006). As can be seen, for any amount of halogen addition, bromine was more effective in oxidizing mercury than chlorine. Mercury oxidation of 80% could be achieved by adding less than 200 ppm of bromine-based additive. An order of magnitude more of chlorine-based additive was needed to achieve the same level of mercury oxidation.

Figure 1-2   Comparison of the performance of bromine- and chlorine-based additives

1.4.3   Conventional air pollution control technologies

1.4.3.1   PM control devices

Fundamental modeling of mercury removal in ESP indicate that mass transfer limitations, even under idealized conditions, greatly restrict the potential for mercury capture by particulate matter collected on electrodes in an ESP (Clack, 2009). ESPs generally remove only PM-bound mercury in the process of collecting PM. PM-bound mercury is preferentially bound to unburned carbon (UBC). Mercury adsorption capacity of inorganic fractions (fly ash) is typically low compared to the UBC present in fly ash. A relationship between the amount of UBC and mercury removal across ESP has been observed for bituminous coal fly ash (Senior et al., 2008). This trend is shown in Figure 1-3 below, showing the percentage capture (percentage of mercury incoming to the ESP) as a function of the amount of UBC. As can be seen, between 20 and 40% mercury capture can be expected in ESP capturing fly ash with about 5% UBC. For higher UBC contents, mercury capture of as much as 80% could be seen.
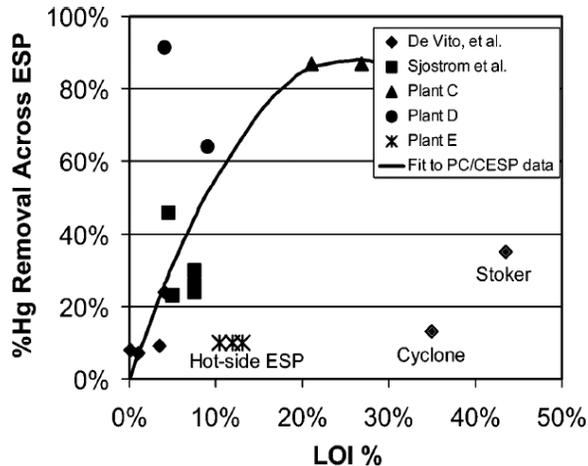
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Figure 1-3   Mercury capture across ESP as a function of the amount of UBC

In addition to the amount of UBC, UBC properties such as surface area, particle size, porosity, and composition may also affect the amount of mercury captured in the ESP (Lu et al., 2007). The study found that while UBC content in fly ash decreased with decreasing particle size, the mercury content of UBC generally increased with decreasing particle size. In addition, the particle size of UBC was found to be the major factor impacting mercury adsorption. Thus, an increased efficiency of an ESP and resultant increased capture of fine fly ash and fine UBC will likely cause a decrease in mercury emissions.

FFs are more effective in removing fine PM than an ESP and they remove gas-phase mercury in addition to PM-bound mercury. Considerably longer contact time between gas phase and fly ash cake in FFs (minutes) than in ESPs (seconds) facilitates adsorption of gas-phase mercury on the fly ash. In addition to longer contact time, better contact is provided in an FF (gas penetrates through the filter cake) than in an ESP (gas passes over the surface of the cake). For example, consistent with earlier ICR effort, a study comparing the capture of mercury in ESPs and FFs in coal-fired power plants in China revealed between 4 and 20% capture in ESPs and between 20 and 80% capture in FFs (Wang et al., 2008).

1.4.3.2   SO$_2$ control devices

In plants with existing wet FGD, the most attractive strategy for mercury control is to increase (and in some cases to preserve) the amount of co-benefit capture. Operation of a wet FGD requires that a PM control device be installed upstream of the wet FGD scrubber (Srivastava and Jozewicz, 2001). As mentioned before, gaseous

compounds of Hg^{2+} are generally water-soluble, and thus wet FGD systems are expected to capture them efficiently. However, gaseous Hg^0 is insoluble in water and therefore does not absorb in FGD slurries. Data from actual facilities has shown that capture of Hg^{2+} in excess of 90% can be expected in Ca-based wet FGD systems, though there are cases where significantly less capture has been measured as a result of unfavorable scrubber equilibrium chemistry (Niksa and Fujiwara, 2004). It has also been shown that under some conditions, Hg^{2+} may be reduced in wet FGD to Hg^0, which could then be re-emitted (Nolan et al., 2003).

When gaseous compounds of Hg^{2+} are absorbed in the liquid slurry of a wet FGD system, the dissolved species are believed to react with dissolved sulfides from the flue gas, such as hydrogen sulfide (H_2S), to form mercuric sulfide (HgS); the HgS precipitates from the liquid solution as sludge. In the absence of sufficient concentration of sulfides in the liquid solution, a competing reaction with sulfites that reduces dissolved Hg^{2+} to Hg^0 is believed to take place. Once this reduction occurs, the newly formed Hg^0 is transferred to the flue gas and increases the concentration of Hg^0 in the flue gas passing through the wet FGD (McDermott, 1999). Hg^{2+} reduction and subsequent Hg^0 re-emission may be more significant in magnesium-enhanced lime (MEL) scrubbers. These scrubbers operate with the much higher sulfite concentration compared to limestone systems (Renninger et al., 2004). In some cases, the reduction of Hg^{2+} to Hg^0, and subsequent re-emission, has been abated with the help of sulfide-donating liquid reagent (EPA, 2002). In addition, transition metals in the slurry (originating from fly ash in the flue gas) are believed to play an active role in the conversion reaction, since they can act as catalysts and/or reactants for reducing oxidized species. There also appears to be increased potential for re-emissions of mercury in wet FGD with appreciable mercury concentrations in the liquor phase (Chang et al., 2008).

1.4.3.3 NO_X control devices

SCR technology has been designed to reduce NO_X through a catalytically enhanced reaction of NO_X with NH_3 reducing NO_X to water and nitrogen. This reaction takes place on the surface of a catalyst, which is placed in a reactor vessel. The reactor ensures that the flue gas is uniformly distributed over the catalyst; it also determines the flue gas velocity. Typical catalyst materials are titanium-oxide and vanadium-oxide on a "coated" substrate structure that may take forms such as plate or honeycomb. Under certain conditions, SCR catalysts have been shown to change

mercury speciation by promoting the oxidation of Hg^0 to Hg^{2+}, particularly for bituminous coal. It should be pointed out that the SCR itself does not remove mercury. Instead, by increasing the amount of Hg^{2+} upstream of the wet FGD, the SCR could improve mercury capture in the wet FGD systems, resulting in the co-benefit removal of mercury (Chu, 2004).

The extent of oxidation of Hg^0 by SCR catalyst and subsequent removal of oxidized mercury in a wet FGD may be affected by chlorine content of the coal, amount of catalyst used to treat the gas stream, temperature of the SCR reaction, concentration of NH_3 and its distribution in the flue gas, and age of the catalyst (Winberg et al., 2004). Oxidation of Hg^0 to Hg^{2+} is greater for bituminous coals than for subbituminous coals. The results of thermochemical equilibrium calculations of mercury species concentration demonstrated that oxidation of Hg^0 to Hg^{2+} with SCR when firing subbituminous coal was limited by equilibrium rather than by kinetics. It follows that, other than altering NO_X control parameters of the SCR, an improvement in oxidation of Hg^0 to Hg^{2+} with SCR on boilers firing low-rank coals is not possible without a change in flue gas chemical composition or without lowering catalyst temperature. Thus, the maximum co-benefit of SCR may be achieved by an appropriate coal-blending. SCR may increase the amount of oxidized mercury up to about 85% and thus improve capture by wet FGD.

1.4.3.4 Co-benefit mercury removal by APCD combinations

When passing across APCDs, part of the Hg_p and Hg^{2+} can be removed. As for the mercury removal efficiency of APCDs, in UNEP's toolkit (2005), 36% for PC+ESP, 74% for PC+ESP+WFGD and 90% for PC+FF were quoted from the ICR report.

The mercury removal efficiencies given by literature were summarized in Figure 1-4. The efficiencies of the most commonly used APCDs including PC+WS, PC+ESP, PC+SDA+FF, PC+ESP+WFGD, PC+SCR+ESP+WFGD, PC+FF, CFB+ESP, CFB+FF, and PC+FF+WFGD 22%, 29%, 59%, 62%, 66%, 67%, 78%, 86%, and 90%, respectively. The combinations of PC+ESP, PC+ESP+WFGD and PC+FF in China have lower mercury removal efficiencies, which is probably caused by Chinese coal quality. According to the analysis of Chinese coals, the chlorine content of Chinese coal is low, resulting in more Hg^0 in flue gas, which is not conducive to mercury removal in APCDs and the average mercury removal efficiencies are thus low.
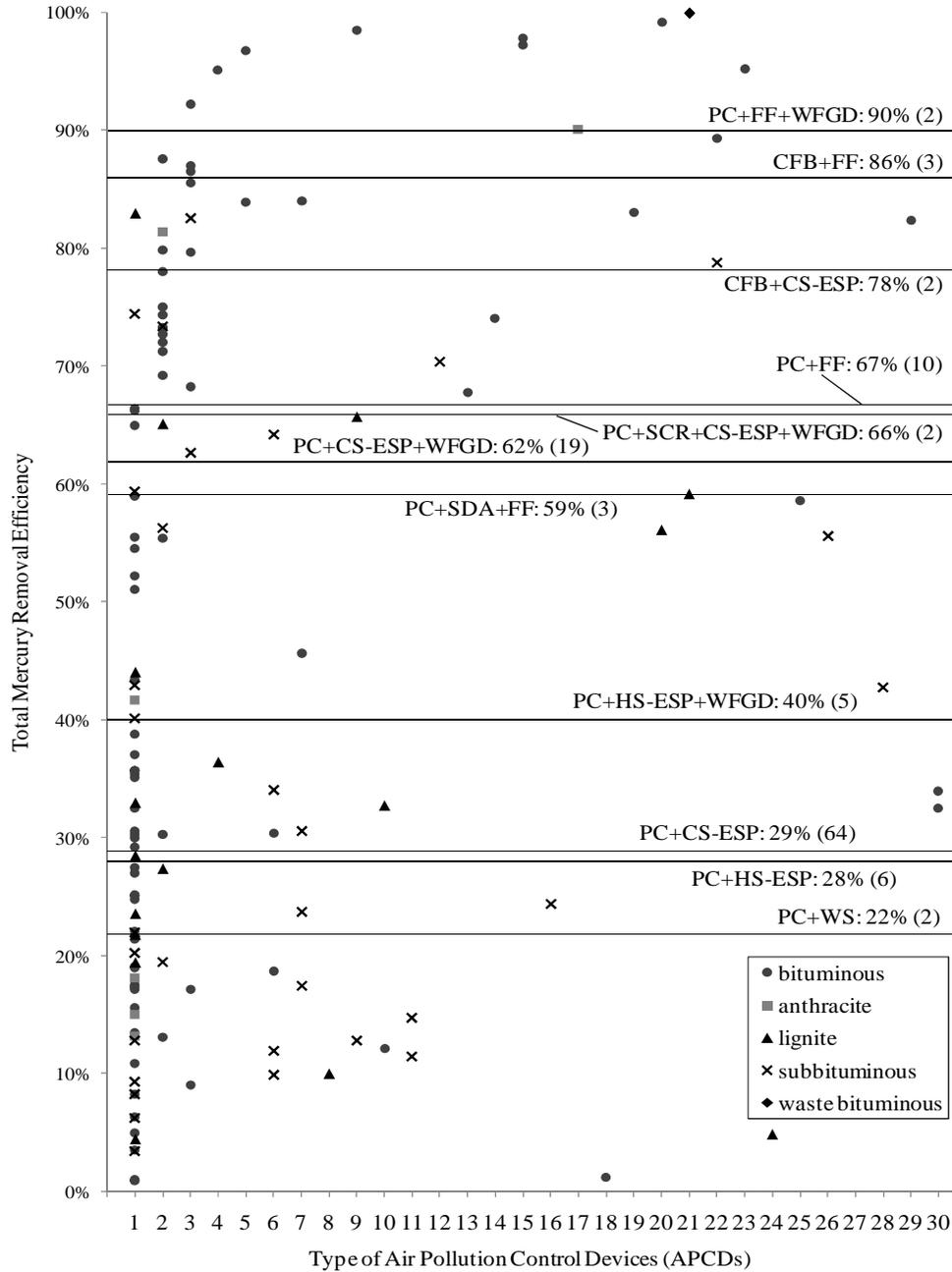
Figure 1-4   Onsite test results for total mercury removal efficiency by APCDs

Note: 1 – PC+CS-ESP; 2 – PC+CS-ESP+WFGD; 3 – PC+FF; 4 – PC+SCR+CS-ESP+WFGD; 5 – PC+FF+WFGD; 6 – PC+HS-ESP; 7 – PC+HS-ESP+WFGD; 8 – PC+CS-ESP+FF; 9 – PC+SDA+FF; 10 – PC+WS; 11 – PC+WS+WFGD; 12 – PC+SDA+CS-ESP; 13 – PC+CS-ESP+CFB-FGD+FF; 14 – PC+SCR+CS-ESP+SW-FGD; 15 – PC+SCR+SDA+FF; 16 – PC+MC+WS+WFGD; 17 – PC+NID+CS-ESP; 18 – PC+SI+CS-ESP; 19 – PC+SNCR+CS-ESP; 20 – CFB+CS-ESP; 21 – CFB+FF; 22 – CFB+SNCR+FF; 23 – SF+SDA+FF; 24 – CYC+CS-ESP; 25 – CYC+CS-ESP+WFGD; 26 – CYC+HS-ESP; 27 – CYC+SDA+FF; 28 – CYC+WS+WFGD; 29 – TUR+CS-ESP+WFGD; 30 – CG.

1.4.4 Dedicated mercury control technologies

1.4.4.1 Activated carbon injection (ACI)

Dedicated mercury control technology is mainly referred to activated carbon injection (ACI) technology. One type is to spray particulate activated carbon (PAC) before PM control devices, mercury is adsorbed onto PAC and removed by ESP or FF downstream; another type is to spray PAC between PM and SO_2 control devices. Currently, ACI technology is already a mature commercial technology, and the use of halogen-treated activated carbon has also started to commercialize. No matter which adsorption method is adopted, the mercury removal efficiency of ACI is mainly affected by physical and chemical properties of the adsorbent, the adsorbent injection rate, flue gas parameters (such as flue gas temperature, flue gas halogen concentration and SO_3 concentration), configuration of APCD and other factors.

In general, higher injection rate of PAC will lead to higher mercury removal efficiency. In some U.S. power plants using sub-bituminous coal, it is found that the mercury removal rate can reach 60% at a certain injection rate of PAC. However, further improvement of PAC injection rate can only bring a small increase of mercury removal efficiency. Previous studies showed that the main factors affecting the mercury removal efficiency of ACI include:

(1) Chlorine content of coal. Generally, bituminous coal contains a higher concentration of chlorine than sub-bituminous coal and lignite. During the coal combustion process, chlorine will evaporate and form free chlorine with oxidizing ability. It is found that adsorption of mercury onto activated carbon is divided into two stages: firstly, elemental mercury in the carbon surface reacts with the free chlorine to form oxidized mercury; then a large amount of oxidized mercury is adsorbed onto the surface of activated carbon. Therefore, burning with low-quality coal, high mercury removal efficiency cannot be achieved due to the limited concentration of free chlorine in flue gas.

(2) Flue gas temperature. The flue gas temperature can significantly affect the adsorption of mercury on activated carbon. In most cases, the flue gas temperature at the inlet of PM control devices is 150°C, at which the adsorption efficiency of the activated carbon is high. However, when the flue gas temperature exceeds 200°C, the mercury removal efficiency of activated carbon will decline rapidly. Generally, the flue gas temperature of the plant with hot side ESP (HS-ESP) using lignite will reach

this temperature range. Acid gases (such as SO_3) are generally considered to be able to compete with mercury on the surface of activated carbon, resulting in the decrease of mercury removal efficiency. Therefore, power plant using high-sulfur coal will face some obstacles in adopting ACI technology.

Since ACI technology is significantly impacted by the chlorine concentration in flue gas, the flue gas SO_3 concentration and flue gas temperature, it is greatly limited in the following situations:

(1) Plants with ESP while burning low-rank coal (such as sub-bituminous coal and lignite). In these plants, the low chlorine content and the relatively high alkali content of coal (calcium and silicon compounds) can cause a very low level of free chlorine in flue gas, resulting in the decrease of Hg^{2+} in flue gas and adsorption efficiency of activated carbon.

(2) Plants with SDA/FF process while burning low-rank coal (such as sub-bituminous coal and lignite). Although the situation in this type of plants is similar to the first case, the main reason for this situation is the use of lime additive, which absorbs most of the free chlorine in flue gas.

(3) Plants burning high-sulfur coal. Since SO_3 competes with mercury on the surface of sorbent, relatively high sulfur content would lead to a decline of mercury adsorption capacity.

(4) Plants with HS-ESP. In these plants, due to the high temperature of ESP, the adhesion of mercury on adsorbent surface decreases, resulting in decreased mercury adsorption capacity.

In the situations above, synergistic mercury removal by conventional APCDs should primarily considered. The combination of WFGD and SCR can achieve high mercury removal efficiency. However, in order to achieve a sounder effect, small doses of ACI could be considered after the flue gas treatment facilities.

In recent years, treated activated carbon technologies are developed. Activated carbon treatment is to improve the functional group and its surrounding structure on the surface of activated carbon, building active sites for specific adsorption processes and thereby controlling its hydrophilic/hydrophobic properties and binding ability with metals or metal oxides. This can be achieved by surface oxidation, surface reduction and metal loading. Generally, the adsorption performance of the treated activated carbon is improved comparing to the original activated carbon.

Common treated activated carbon includes those carrying chlorine, bromine and iodine. For example, when using $CuCl_2$ impregnated activated carbon, chlorine atoms released from the surface of activated carbon bind with Hg^0 to form HgCl (g), part of which further turns into a more stable mercury compound $HgCl_2$. The adsorption process consists of both physical and chemical adsorption processes. In addition, the oxidizability of chlorine is stronger than sulfur, so chlorine containing activated carbon has a better ability of mercury adsorption than sulfur containing activated carbon. At 140°C, the ability of Hg^0 adsorption is as follows: untreated activated carbon < sulfide or sulfur containing activated carbon < chlorine containing activated carbon < bromine containing activated carbon.

Treated activated carbon can significantly improve mercury removal efficiency. Figure 1-5 shows the comparison of mercury removal efficiencies of untreated and treated activated carbon with various coal types. Treated activated carbon can achieve high mercury removal efficiency even when the coal rank is low. Meanwhile, for high-rank coal, treated activated carbon can greatly improve the efficiency of mercury removal and thus reduce the consumption rate of activated carbon.
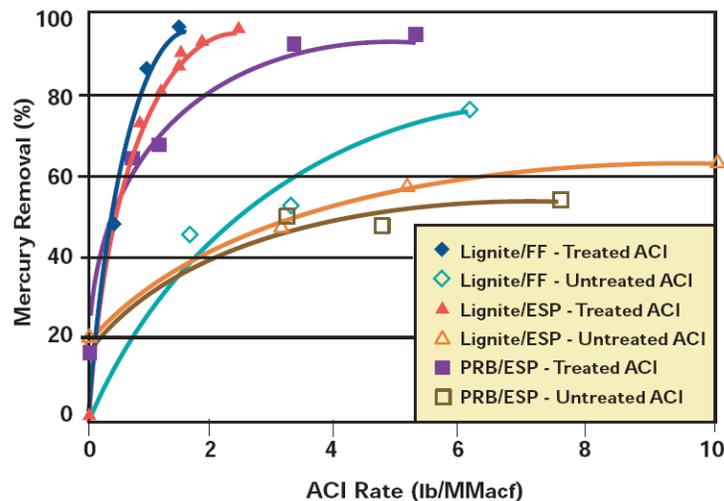

Figure 1-5   Mercury removal efficiencies of untreated and treated ACI

1.4.4.2 TOXECON technology

When applying mercury adsorbents, the mercury-bonded adsorbent will deposit onto the fly ash, which reduces the market value of fly ash for cement production. To solve this problem, a TOXECON mercury removal technology was developed. In

TOXECON process, activated carbon is injected after PM control devices, and a baghouse is immediately followed. In TOXECON technology, fly ash is mainly removed by PM control devices, while the mercury adsorbent is mainly captured by the baghouse. In some experiments, TOXECON with bromine containing activated carbon under the injection rate of 1.2 lb/Mmacf can achieve mercury removal efficiency of more than 90%. Figure 1-6 shows the principle of TOXECON.
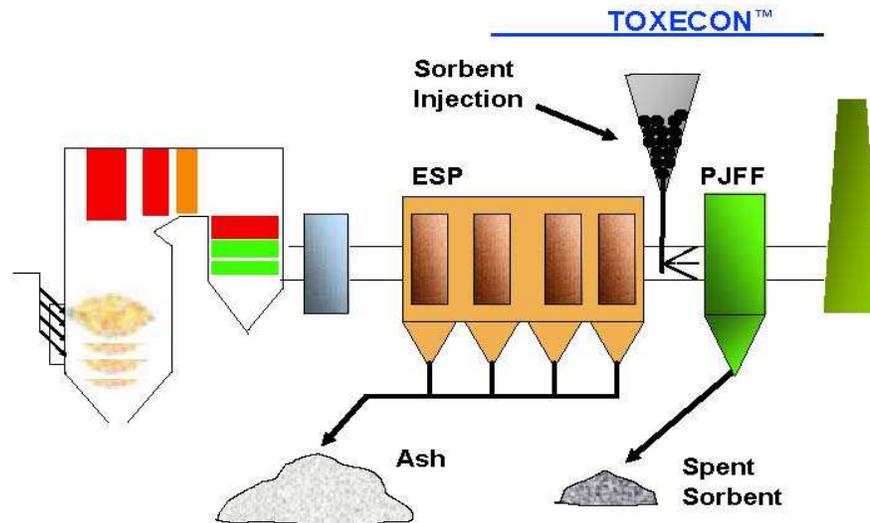

Figure 1-6   Flowchart of TOXECON technology

1.4.4.3 Influence of ACI on power plants

ACI technology has broad application prospects, but attention should also be paid to its impact on the operation of the plant. So far, no data indicates significant impacts of ACI technology on the plant. However, some of the adverse effects are accumulated in the operation, so long-term observation is needed.

Impact on the operating load of PM control devices. Impact of ACI technology on power plants is mainly revealed in the PM control devices. It was found in actual operation that ACI technology slightly increases the operating load of PM control devices, usually less than 4%, and lower load growth in the use of treated ACI.

Activated carbon injection at the inlet of small-scale CS-ESP will lead to the increase of discharging rate of ESP arc: arc discharging rate increased from <1 time per minute to >10 times per minute. Arc discharging rate is an important indicator of the performance of ESP, but the mechanism is not yet clear and still needs long-term experiments.

For plants with TOXECON technology or SDA+FF, the frequency of bag filter deashing will increase due to the injection of activated carbon. This has been confirmed in the field tests.

1.4.5　Multi-pollutant control technologies

Conventional pollutant control technologies mainly use separated devices for different types of pollutants. Multi-pollutant control technology is designed to achieve various pollutant removal by one control device. Currently, multi-pollutant control technology is still in the laboratory stage, not yet applicable for commercial use.

1.4.6　Treatment and reutilization of byproducts from coal combustion

In the process of flue gas treatment, part of the flue gas mercury enters the coal byproducts, including bottom ash, fly ash, FGD gypsum and waste water. Previous studies show that the mercury concentration level in coal byproducts is significantly higher than the earth crust. Therefore, there are cross media impacts of mercury in coal-fired power plants and industrial boilers. In the stockpiling or reutilization processes of coal byproducts, there could be risks of secondary mercury releases due to the leaching or high temperature processes.

1.4.6.1　Coal ash

Coal ash is the residue from pulverized coal combustion, 80% of which is fly ash and 20% is bottom ash. Fly ash can be reused in areas such as building materials and agriculture. In the field of building materials, it is mainly used in construction, road works and backfilling. In agriculture, it is mainly used for soil reclamation, soil improvement and fertilizer production.

Studies show that more than 98% of the mercury releases into the flue gas when fly ash is used in cement production. In brick production using fly ash, $HgCl_2$ (Hg_2Cl_2) almost completely releases, HgS partially releases, and HgO remains the same. Because of different types of mercury compounds in the original samples, mercury release rate varies between 1.5-49.3%. Therefore, we should pay attention to the mercury emissions in fly ash reutilization (Wang et al., 2013).

During the stockpiling process of fly ash, the mercury concentration in leachate is much lower than the national drinking water standard. Therefore, fly ash in stockpiling will do no harm to the environment (Wang and Meng, 2012).

1.4.6.2　FGD gypsum

Limestone - gypsum WFGD technology is the most widely used desulfurization technology around the world. This technology will generate a large amount of FGD gypsum. Currently, there are two main ways to comprehensively reutilize byproduct gypsum: first, as cement retarder, and second for building materials, including gypsum board, gypsum block, gypsum hollow lath, dry mortar and gypsum brick. In addition, gypsum is gradually being applied in agriculture.

Gypsum will release 11–55% of the total mercury during the board making process, $HgCl_2$ content is an important factor affecting mercury release (Liu et al., 2013). High temperature reutilization of coal byproducts should be controlled to reduce secondary mercury release.

1.5 Mercury emission control regulations and standards for coal-fired power plants and industrial boilers in China

China has the largest coal consumption in the world. In 2010, the amount of national coal consumption was over 3.3 billion tons, where coal consumption in the power sector reached 1.6 billion tons. Coal combustion is the largest source of atmospheric mercury emissions in China.

China has paid great attention to atmospheric mercury emission control for coal combustion. In 2009, the State Council released the "Notification from State Council to the Ministry of Environmental Protection and Other Departments on the Guidance of Strengthening of Heavy Metal Pollution Prevention and Control", and stressed the mercury pollution prevention to be a priority. In May 2010, they released the "Notification from State Council to the Ministry of Environmental Protection and Other Departments on the Guidance of Promoting Joint Prevention and Control of Air Pollution to Improve Regional Air Quality", and further proposed the construction of the demonstration projects for synergistic multi-pollutant control for thermal power units, including flue gas desulfurization, denitrification, dedusting and demercuration.

In September 2010, Ministry of Environmental Protection launched a pilot project on atmospheric mercury pollution control of coal-fired power plants, and conducted mercury monitoring work with joint efforts from five major power groups.

In the "Twelfth Five-Year Plan on Control of Heavy Metal Pollution", mercury was listed as a key pollutant, and coal is included in the key sector for mercury

emission control. By 2015, mercury emissions from key regions should be abated by 15% than those in 2007.

Ministry of Environmental Protection issued the new "Air Pollutant Emission Standards for Thermal Power Plants" (GB 13223-2011) on July 29, 2011. The new standards tightened the requirements of PM, SO_2 and NO_x emission control in thermal power plants, and for the first time added the limits of atmospheric mercury emission. It is required that atmospheric mercury emission from coal-fired power plants should attain the concentration standard of 0.03 mg/m^3 by 1 January 2015. The newly released standards for thermal power plants play an important role in promoting atmospheric mercury emission control.

2 Nonferrous metal smelting process (Zinc, Lead, Copper and Industrial Gold)

2.1 Nonferrous metal smelting process

The nonferrous metal smelting processes controlled by the convention include the smelting and roasting process during the production processes of zinc, lead, copper and industrial gold.

2.1.1 Zinc smelting process

The common zinc concentrates used during zinc production process are the zinc sulfide concentrate, which are obtained from sphalerite through foam floatation. Other renewable materials such as zinc oxidize can also be processed as the raw materials for zinc smelting process.

Zinc smelting processes in China can be divided into two major types, namely the pyrometallurgical process and the hydrometallurgical process. The pyrometallurgical process, where metallic zinc is extracted from zinc oxide materials with carbon as reducing agent at high temperature, can further be divided into the imperial smelting process (ISP), the vertical retort zinc smelting process (VRZSP), the electric zinc furnace (EZF), and various artisanal zinc smelting processes (AZSP). With the hydrometallurgical smelting process, the zinc concentrates are firstly roasted to make zinc calcine. The zinc calcine is then leached with acid solution. The metallic zinc metal is finally produced after purification and electrolysis. The flow diagram of zinc production process is shown in Fig. 2-1.
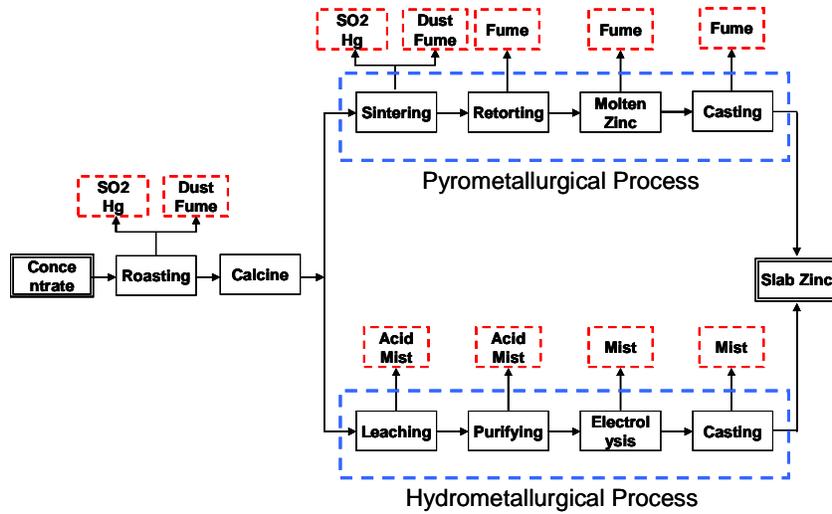
Fig. 2-1 Flow diagram of zinc production process

2.1.2 Lead smelting process

Lead smelting process refers to the process that lead sulfide is oxidized into lead oxides and then reduced into metallic lead with carbon at high temperature. This process can be divided into two process of crude lead smelting and refining. However, a large part of mercury is emitted into atmosphere during crude lead smelting process.

The crude lead smelting process refer to the processes including lead concentrates oxidation, lead calcine reduction, lead sludge separation. The flow diagram of lead production process is shown in Fig. 2-2.

Fig. 2-2 Flow diagram of lead production process

The smelting reduction processes include oxygen-rich bottom blowing smelting-melting rich lead sludge direct reduction process, oxygen-rich bottom blowing smelting-blast furnace reduction technologies (Shuikoushan smelting

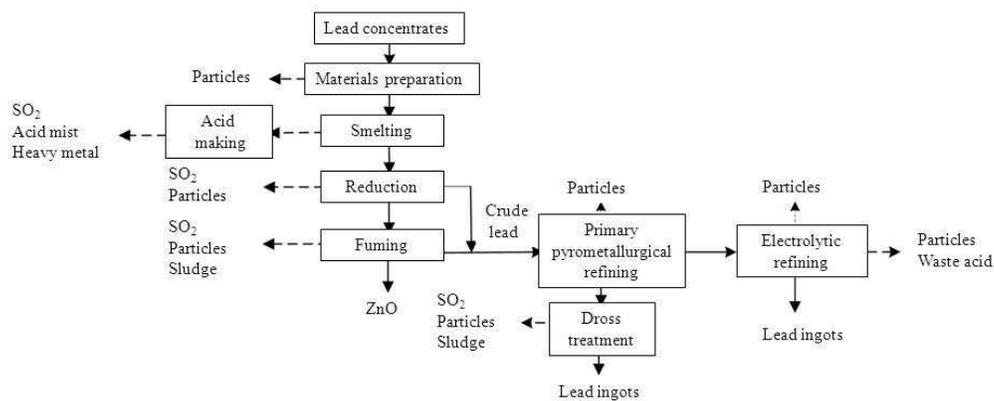technology), oxygen-rich top smelting-blast furnace reduction technology, sintering-closed blast furnace smelting technology (ISP), oxygen bottom smelting technology (QSL) and Kaldor furnace smelting technology.

Fuming processes include rotary kiln technology, fuming furnace technology, fuming furnace-waste heat boiler integrated technology.

2.1.3 Copper smelting process

The raw materials for copper smelting include native copper, sulfide ore and oxide ore. The sulfide ore is the main material for copper smelting process. The copper smelting processes can be divided into pyrometallurical process and hydrometallurgical process. The former one is the main technology in China. The production of copper making with pyrometallurigical process took up 85% of the total production in China. The hydrometallurgical process is being gradually extended nowadays, which largely decrease the cost of copper smelting.

The main kinds of furnace for pyrometallurgical smelting include sinter smelting furnace, reverberatory furnace, electric furnace and flash furnace. The copper matte produced from smelting furnace was converted into crude copper in the convertor. The crude copper was then refined in the refining process or electrolyzed after being casted into positive plate, so as to obtained electrolytic copper (containing 99.9% of copper). During the smelting and converting process, mercury will emit into atmosphere. The hydrometallurgical processes include roasting-leaching-electrolyzing process, leaching-extraction-electrolyzing process, bacterial leaching process. These processes are used to leach complex low-grade ore, copper oxide and copper ore waste.

The main copper smelting processes used in China can be divided flash furnace smelting process (FFSP), rich-oxygen bath smelting process (RPSP), imperial furnace smelting process (IFSP), roasting-leaching-electrolyzing process (RLEP) and electrolytic furnace/reverberatory furnace process (EF/RF).

2.1.4 Industrial gold smelting process

The atmospheric mercury was emitted from the process to treat refractory gold concentrates. The reserve of refractory gold concentrates was regarded to be about 1/3 of total proven reserves of gold concentrates. The main process for refractory gold concentrates include biological oxidation, pressure thermal oxidation, roasting oxidation pretreatment process. The main process caused atmospheric mercury

emission was the roasting-cyaniding gold extraction process.

The roasting-cyaniding gold extraction processes refer to the cyaniding process after roasting gold concentrates. The fluidized-bed roasting was used for concentrates roasting with the processing capacity of 5000~6000 t/d. The temperature of the roaster was about 650℃-750℃. A typical flow diagram of this process was shown in Fig. 2-3.
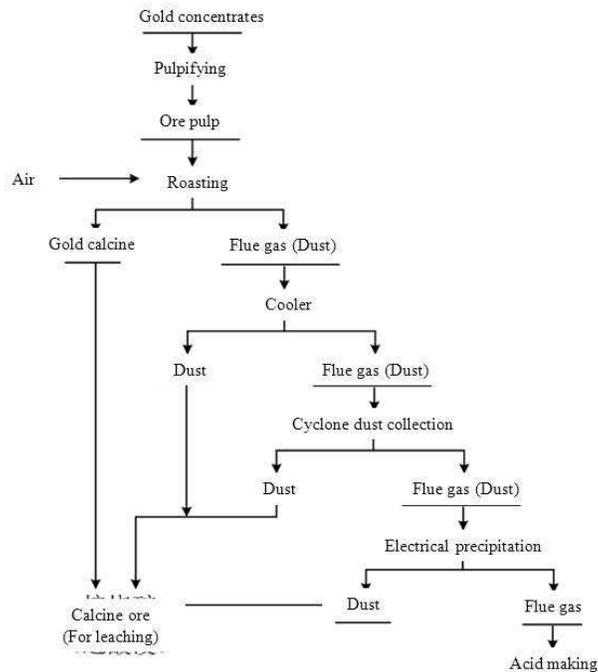
Fig. 2-3 Flow diagram of roasting process

2.2 Atmospheric mercury emission from nonferrous metal smelters

Trace amounts of mercury was often associated in nonferrous metal ores. Song et al., (2010) and Li et al., (2010) estimated mercury concentration in the zinc concentrates and found out that mercury concentration in ore concentrates varies with place. For example, mercury concentration in the zinc concentrates from Xizang province was only 0.23 mg/kg while the concentration in the concentrates from Gansu reached 500 mg/kg. Wu et al., (2012) summed mercury concentration in 351 zinc concentrates, 190 lead concentrates and 174 copper concentrates and found out their concentration varied from 0.01 to 2000mg/kg.

During the high temperature roasting process, most of mercury will emitted into

flue gas. The emitted flue gas was distributed into other materials such as dust, waste acid and sulphuric acid, after dust collector (DC), flue gas scrubber (FGS), electrostatic demister (ESD). Only a small amount of mercury will be emitted into atmosphere.

Compared to the emission amount of SO_2, NO_x, and particulate, mercury concentration in the flue gas was quite low ($\mu g/m^3$ degree). Thus, the difficulty as well as cost of field measurement of mercury will be higher. In order to increase the understanding to atmospheric mercury emission from nonferrous metal smelters, filed measurement of atmospheric mercury emission from single smelter is encouraged. However, it is impossible to measure atmospheric mercury emission from all nonferrous metal smelting facility.

In most situation, atmospheric mercury emission was estimated with emission factor method. In earlier estimates, the mercury emission factors for China's nonferrous metal smelters were regarded as same as those for other countries (Nriagu et al., 1988; Pacyna et al., 1996). Pirrone et al. (1996) assumed the mercury emission factors for zinc and lead smelters in developing continents to be 25 and 3 g/t metal produced, respectively. But there were no data for developing countries including China. Wu et al. (2006) and Wang et al. (2006) analyzed the mercury content in concentrates and estimated the mercury emission factor to be 13.8-156.4, 43.6 and 9.6 g/t for zinc, lead and copper smelters, respectively. However, these values were proven to be overestimated since the synergic mercury removal effect of APCDs was not considered (Feng et al., 2004; Li et al., 2010; Wang et al., 2010; Zhang et al., 2012). Feng et al. (2009) summarized previous studies and pointed out that the average emission factors were 5.4-155 g/t Zn, 43.6 g/t Pb, 9.6 g/t Cu, respectively. Wu et al., (2012) summed a research table according to current researches.

Current researches on gold smelting are much limited. The emission factor for industrial gold smelting is 0.02-0.79 g/g (Kim et al，2010; Lacerda，1997; Lacerda and Marins， 1997; Nriagu & Jerome O，1993; Pacyna et al.，2010; Pirrone et al.，2009; Steets et al， 2011). However, these emission factors are mainly from amalgamation production and lack the support of experimental data.

Caused by the large uncertainty of emission factor method, another method based on technology process was developed. This method requires to considering many parameters such as mercury input during smelting process as well as mercury removal efficiency of air pollution control devices.

Table 2-1 Mercury emission factor for zinc, lead and copper smelters

Metal	Smelting Process	Mercury emission factor (g t^{-1})												
		A[a]	B[a]	C[a]	D[a]	E[a]	F[a]	G[a]	H[a]	I[a]	J[a]	K[a]	L[a]	M[a]
Zinc	-[b]	8-45	25	20		13.8-156.4	7.5-8	16.61	5.4-155	7				7.82
	EP with MRT										5.7	0.5		0.59
	EP without MRT										31		0.57	9.75
	RZSP										34			6.16
	EZF													13.80
	ISP										122		2.98	6.02
	AZSP				79/155						75			45.75
Lead	-[b]	2-4	3	3		43.6	3	14.91	43.6	3				10.97
	RPSP												1.00	1.19
	SMP												0.49	10.16
	SPP													29.35
	ISP													6.07
Copper	-[b]			10		9.6	5-6	6.72	9.6	5				0.85
	FFSP												0.23	0.26
	RPSP												0.09	0.28
	IFSP													1.07
	EF/RF													14.96
	RLEP													0.38

a. A. Nriagu et al., 1988; B. Pirrone et al.,1996; C. Pacyna et al., 2002; D. Feng et al.,2004; E. Streets et al.,2005;Wu et al.,2006; F. Pacyna et al., 2006; G. Hylander and Herbert., 2008; H. Pacyna et al., 2010; I. Feng et al., 2009; Li et al.,2010; K. Wang et al., 2010; L. Zhang et al., 2012; M. Wu et al., 2012

b. Not specific value for each process

2.3 The best environmental practice for atmospheric mercury emission from nonferrous metal smelters

The best environmental practice for controlling atmospheric mercury emission nonferrous metal smelting process is as follows.

- Enforcement of the operational management; establishment of post procedures; development of contingency plans; regular training of the operators.

- Enforcement of the use and maintenance of production equipment so as to ensure the normal operation of equipment.

- Pay attention to mercury measurement and management; take regular mercury balance test in the whole plant.

- Establish atmospheric mercury accounting system such as mercury generation and emission system.

- Establish and improve the recording and production management systems.

- Take reliable measurements to prevent flue gas condensation and pipeline corrosion when using baghouse or electrostatic precipitators.

- Operate the dust removal system under vacuum so as to avoid overflow of harmful gases.

- Dispose waste reasonably to prevent secondary pollution.

2.4 Atmospheric mercury emission control technologies in nonferrous metal smelters

2.4.1 Adjustment of industrial structure

Atmospheric mercury emission can be reduced by limiting and eliminating backward production capacity and increasing the threshold of the establishment of a new smelting enterprises including the application of advanced technologies and supporting air pollution control devices.

Wu et al., (2012) pointed out that atmospheric mercury emission factor reached 45.75 g/t for artisanal zinc smelters while the emission factor was only 9.75 g/t for hydrometallurgical process. For lead smelters, the atmospheric mercury emission factor reached 29.35 g/t for artisanal lead smelters while the emission factor was only 1.19 g/t for rich-oxygen bath smelting process. In copper smelting industry, the emission factor of electric furnace and reverberatory furnace (14.96 g/t) was also

higher than flash furnace smelting process and rich oxygen bath smelting process (0.26-0.28 g/t)

2.4.2 Synergic atmospheric mercury control technology

Generally, air pollution control devices (APCDs) for primary flue gas in most nonferrous metal smelters consist of dust collectors (DC) and acid plants.

2.4.2.1 Dust collector

Dust collectors installed in zinc smelters generally included cyclone dust collectors, waste heat boilers, and electrostatic precipitators. Some smelters installed fabric filters.

Mercury concentration in the flue gas from roaster generally varies in a large range. Sometimes, the concentration reached as high as $10mg/m^{3.}$

Dust collector generally remove only particulate matter (PM)-bound mercury by collecting PM. Current research in nonferrous metal smelters indicated that the WHB and CYC has low mercury removal effiency, generally under 5% (Zhang et al., 2012). The ESP has Hg removal efficiency from 2.39% to 20.4%. The effiency of FF is higher, from 25.21% to 56.10% (Li et al., 2010; Wang et al., 2010; Zhang et al., 2012).

2.4.2.2 Acid plant

Different SO_2 treatment processes are generally used depending on SO_2 concentration in the flue gas. Flue gas desulfurization and sulfuric acid production are the two main methods of SO_2 treatment.

When SO_2 is lower than 2.5%, the flue gas desulfurization method is adopted for flue gas treatment. For flue gas with a SO_2 content between 2.5% and 3.5%, two kinds of acid making methods can be used. One is non-steady-state method with the conversion ratio of 80–90%. Thus, the flue gas should be treated with additional FGD so as to emission on standard. The other method is the WSA method from the Danish company Topsoe. This method requires 3.5% of SO_2 concentration in the flue gas to ensure stable operation. When SO_2 concentration is in the range of 3.5–5.0%, single convection and single adsorption method, matching with waste flue gas adsorption equipment, can be used to ensure the emission on standard. When SO_2 concentration is larger than 5.0%, regular double convection and double adsorption method can be adopted.

The mercury removal inside the acid plant can be generally divided into two stages. During the first stage, that is, FGS and ESD, mercury in the flue gas goes into the waste water. During the second stage, that is, DHT and the C&A process, mercury in the flue gas goes into the sulfuric acid product. The removal efficiency in first stage is determined by the speciation of mercury in the flue gas entering into the acid plant. Field experiment in 7 nonferrous metal smelters, including the one reported in this project indicated that the Hg removal efficiency of FGS is 17.40-66.59% while the removal efficiency of ESD is 30.3-32.3%. The Hg removal efficiency for the second stage depends on acid making process. For SCSA process, the removal efficiency is about 55.41% while the removal efficiency for DCDA is from 68.38 to 99.64%.

2.4.3 Specific mercury control technologies

The specific mercury control techonologies in the world can be divided into Boliden-Norzink process, Outokumpu process, Bolkem process, Selenium filter process, Selenium filter process, Activated carbon process, Lurgi application process, Tinfos Miltec process, and DOWA filter process。

2.4.3.1 Boliden-Norzink process

The Boliden-Norzink mercury removal process is a continuous gas scrubbing process, which removes mercury from the flue gas using an acidic mercuric chloride ($HgCl_2$) solution. Oxidized mercury (Hg^{2+}) in the $HgCl_2$ solution reacts with elemental mercury (Hg^0) in the flue gas and rapidly generates water-insoluble solid mercurous chloride (Hg_2Cl_2). Some of this Hg_2Cl_2 is used to generate the $HgCl_2$ solution, added to supply Hg^{2+} ions, while the rest is recycled following precipitation treatment. The Boliden-Norzink process involves the following three steps. First, mercury scrubbing occurs in the reaction tower. The reaction tower is a counter-current absorber tower made of fiber glass reinforced polypropylene plastic. In the reaction tower, the $HgCl_2$ solution is sprayed evenly in the packing area and reacts with mercury in the flue gas. The second step involves the production of the calomel mercurous chloride (Hg_2Cl_2), which is suspended in solution. Some of the Hg_2Cl_2 is also sent to chloride process. During the final step the Hg_2Cl_2 is oxidized by Cl_2 in the stirring tank.

2.4.3.2 Outokumpu process

The Outokumpu process is based on converting the elemental mercury in the gas into a sulfate according to the reaction:

$$Hg + H_2SO_4 \text{ --> } 1/2\ O_2 + HgSO_4 + H_2O$$
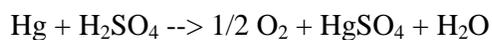
2.4.3.3 Bolkem process

The Bolkem process is based on mercury being reacted with sulphuric acid and treated with sodium thiosulphate to precipitate the mercury as mercuric sulphide.

2.4.3.4 Selenium filter

The selenium filter is especially suited for low mercury concentrations in the gas and consists of a porous inert material soaked with selenious acid which is then dried to precipitate red amorphous selenium according to the reaction: $H_2SeO_3 + H_2O + 2SO_2 \text{ --> } Se + 2\ H_2SO_4$. The filter will remove approximately 90% of the incoming mercury. The investment cost is proportional to the gas flow rate.

2.4.3.5 Selenium scrubber

The selenium scrubber, like the selenium filter, relies on the presence of amorphous elemental selenium to react with the elemental mercury in the gas. The selenium scrubber is suitable for removing relative large quantities of mercury in the gas and has a removal efficiency of approximately 90%.

2.4.3.6 Activated carbon filter

The activated carbon filter is well known for its adsorption properties. For the adsorption of mercury, activated carbon can normally adsorb 10-12% of its own weight. The operating temperature of the carbon filter is limited to 50°C. The method is especially suitable for low mercury concentrations in the gas. A 90% removal efficiency is normally achievable.

2.4.3.7 Lurgi application

The Lurgi application is a kind of activated carbon filter. Lurgi consists of mercury removal units (MRU) which uses wet ESP and a packed bed absorber using sulphur-impregnated coal to remove mercury from the off-gas. The wet ESP removes dust and tars before the mercury contaminated off-gas is heated to 60-85oC and is absorbed in series of packed bed absorbers. In order to control the gas flow through the unit, the MRU is equipped with a system for pressure control. The MRU has a removal efficiency of 95%.

2.4.3.8 Tinfos Miltec process

The Tinfos Miltec process removes mercury from the off-gas by washing

it con-currently with seawater containing sodium hypochlorite which oxidizes the mercury. In addition, the wash water collects dust, and reduces sulphur dioxide (SO2) emissions to air. The wash water after gas cleaning contains the mercury as mercury salts, which is added disodium sulfite (Na2S). This leads to the formation of mercury sulfate (HgS) and other metal sulfite precipitate, which can be removed from the process using a press filter. The Miltec process removes 95 % of the mercury from the off-gas.

2.4.3.9 DOWA filter process

The DOWA filter process (lead (II) sulfide covered pumice filter) captures

metallic, oxidized and particulate mercury.

The mercury removal efficiencies of specific mercury control devices was impacted by the flue gas component as well as flue gas concentration. The suitable specific air pollution control device will have the mercury removal efficiency of more than 90%. Field experiment in a Chinese zinc smelters installing with Boliden-Norzink mercury removal technology indicated its mercury removal efficiency of 88-92%. Table 2-2 shows the mercury removal efficiencies of typical mercury removal technologies tested in Sweden Boliden smelters

Table 2-2 Mercury removal efficiencies of typical mercury removal technologies tested in Sweden Boliden smelters

Mercury removal techniques	Flue gas flow	Total mercury concentration (Hg-tot)		
		$\mu g/Nm^3$	$\mu g/Nm^3$	Reduction efficiency %
Boliden Norzink process	9879	9879	30	99.7
	51	51	13	74
Dowa filter	50	50	1.4	97
	10.5	10.5	1.2	88
Selnium filter	1008	1008	48	95
	42	42	12	71

Active carbon filter	1206	1206	32	97
	37.2	37.2	2.7	93

2.4.4 The treatment and reuse of byproduct from nonferrous metal smelting process

Mercury releases from concentrates into flue gas at high temperature. The released mercury would be distributed into fly ash, waste acid and sulfuric acid at dust collector, flue gas purification and acid making process. The disposal of these mercury-contained materials will lead to mercury emitting into environmental materials. During the gold, lead and copper smelting process, the fly ash captured by the dust collector would be resent to roaster/smelting furnace. Thus, mercury in the fly ash is released into flue gas again. The disposal of fly ash descried above is one of the pathways to treat fly ash in the zinc smelters. However, in most zinc smelters, fly ash is leached in the leaching process with zinc calcine. Therefore, mercury in the fly ash would contaminate next production process. Some part of mercury flow into the leaching process would go to volatilization kiln with leaching sludge and released into flue gas again. Other part of mercury would go to heavy metal sludge such as silver sludge and cadmium sludge during the purification of leachate. Thus, during the disposal of fly ash, the transportation of mercury into lower production process should be avoided. This could be achieved by disposal fly ash after distilling the mercury in it or avoiding the reuse of fly ash in the leaching process.

The waste acid is one of the main outputs of mercury inputted into smelters. During the production process, the waste acid with high mercury concentration should be avoided mixing with other kind waste water. The waste acid sludge from filter pressing waste acid contains high concentration of mercury (generally more than 1%). Thus, they are much easier to be recycled. However, when the waste acid mixes with other kind of waste water, mercury concentration would be lower. Thus, the sludge from this kind of water would not be high enough to be recycled. Besides, since the sludge contains certain amount of mercury, it is also hard to be reused in other kinds of industry. Moreover, the waste water should be avoided reusing in the leaching process before removing mercury in it.

Sulfuric acid is one of the main outputs during metal producing process. The sulfuric acid is generally used in the fertilizer and chemical industry. Since the flow of sulfuric acid from nonferrous metal smelters is still unknown. Thus, most mercury in

the acid should be removed to avoid its transportation to the downstream production units.

2.5 Atmospheric mercury emission control regulations and standards from nonferrous metal smelting industry

In 2010, the zinc, lead, copper and gold production reached 5210 kt, 4160 kt 4540 kt and 342 t in China (Jia and Wang, 2011；Chinese gold industrial association, 2011).

2.5.1　Industrial restructuring

China has promulgated a series of notifications to restructure industrial, such as "Catalogue of industrial structure adjustment (2005)", "Catalogue of industrial structure adjustment (2011)", "Notice on the guidance of regulating the behavior of lead and zinc industry investment and accelerating structural adjustment" "the state council on further strengthening elimination of backward production capacity". The flowing zinc, lead and copper producing processes are included in the elimination directory: "The zinc roasting furnace or oxidized zinc production process with simple dust collection facilities, such as muffle furnace, manger furnace, horizontal tanks and small vertical retorting furnace", "The lead smelting furnace such as sinter pot, sinter plate, and simple blast", "The copper smelting furnace such as blast furnace, electric furnace and reverberatory furnace", "The gold smelting process such as gold amalgamation, small cyanide pool leaching process and artisanal gold production process".

The ministry of industry and information technology of the People's Republic of China issued the target of eliminating backward production capacity in key industries during the "12th Five-Year Plan" and pointed out that China will eliminated 650 kt zinc backward production capacity, 1300 kt lead backward production capacity and 800 kt copper backward production capacity from 2010-2015.

"The access conditions for lead and zinc industry (2012)", "The access conditions for copper industry (2013)" also proposed requirements for new smelters. On the one hand, the production of refined copper, lead and zinc should be limited in 6500 kt, 5500 kt and 7200 kt during the 12th Five-Year period, and the relative increase ratio should be controlled in 7.3%, 5.2%, and 6.9% respectively. On the other hand, the requirement on the smelting technology and environmental protection has

been strengthen. For the new lead smelting project, the smelting process should adopt the advanced lead smelting process, such as oxygen-rich bottom blowing strengthen melting-liquid high lead sludge direct reduction process, one-step lead smelting process, or oxygen-rich top blowing strengthen melting process. Besides, acid plants with the double conversion double adsorption or other dual-adsorption acid making system should be installed for the smelting flue gas. For the new zinc smelting project, the boiling fluidized roasting process with high sulfur utilization rate and exhaust emission on standard should be installed for sulfur zinc roasting. The square for single boiling fluidized bed must be no less than 109 m^2. According to SO_2 concentration in the flue gas, plants with acid making of double conversion double adsorption, exhausted gas adsorption or their combination should be installed. For new copper smelting project, advanced technology with high production rate, low energy consumption, standard environmental protection practice and good utilization of resources should be adopted. Acid making plants, resources utilization units, energy saving equipment should be installed. The acid plants should be installed with dilute sulfuric acid scrubber and purification units, double conversion and double adsorption (or triple conversion and triple adsorption) units. Water or hot concentrated acid are prohibited to be used in purification units. Treatment facilities are required to set up for sulfuric exhaust.

Except for industrial restructuring, China also issued many relative standards on mercury emission limits and technical policy guidance.

2.5.2 Atmospheric mercury emission standards for zinc and lead smelting industry

The "Emission standard of pollutants for lead and zinc industry (GB25466-2010)" proposed that atmospheric mercury emission limit for smelting/roasting flue gas from all lead and zinc smelters is 50 μg/m^3. Atmospheric mercury concentration around the boundaries of corporate should be less than 0.3 μg/m^3. The "Industrial pollution control technology policy for lead and zinc smelting industry (2012)" points out that SO_2 in the smelting/roasting flue gas should be recycled to produce sulfuric acid or other products. The acid making technologies of adiabatic evaporation acid purification method and double contacts method are encouraged to be used. Measures should be used to remove acid mist and other exhausted gas to purify flue gas. The acid mist from electric tank in the hydrometallurgical process should be collected and purified. Zinc leaching tank and purification tank should be supported with waste gas collection, gas-liquid separation

and mist removal equipment. Specific mercury removal technologies such as chloride and iodide method are encouraged to be used to remove mercury in the flue gas.

2.5.3 Atmospheric mercury emission standards for copper smelting industry

The "Emission standard of pollutants for copper, nickel and cobalt industry (GB25467-2010)" proposed that atmospheric mercury emission limit for the flue gas from all copper smelters is 12 μg/m^3. Atmospheric mercury concentration around the boundaries of corporate should be less than 1.2 μg/m^3.

2.5.4 Atmospheric mercury emission standards for gold smelting industry

The "Integrated emission standard of air pollutants" proposed that atmospheric mercury emission limit for the flue gas from gold smelters is 15 μg/m^3. Atmospheric mercury concentration around the boundaries of corporate should be less than 1.55 μg/m^3.

3 Cement manufacturing process

3.1 Process

3.1.1 Introduction

The basic chemical principles of cement production are as follows: $CaCO_3$ is firstly decomposed to CaO and CO_2 at 900°C, which is called calcination. Subsequently the clinker containing silicate, aluminate and calcium ferrite is produced through the reaction of CaO, SiO_2, Al_2O_3 and FeO at the temperature of 1400-1500°C. Finally the clinker, plaster and other additives are milled to produce cement.

Cement kiln is the main facility in cement manufacturing process, including rotary kiln and shaft kiln. Rotary kilns can be classified as precalciner process, preheat process, heat recovery kilns, dry kilns, Lepol kilns and wet rotary kilns. Shaft kilns include conventional shaft kilns and mechanized shaft kiln. The precalciner process accounts most in cement production.

The cement production of China in 2010 is 20.9 billion tons, and the precalciner process, rotary kilns and shaft kilns contribute 80%, 1% and 19%, respectively.

3.1.2 Rotary kilns

Raw materials, called slurry in wet process, is heated in rotary kiln, which is a large, constantly rotating and tilting steel furnaces. The air and raw materials flows in opposite directions in rotary kilns to make the heat transfer easier. Raw materials enter the rotary kiln through the higher end, or cold end, and flow to the lower end. Coal and fuel is usually used as fuel to heat the rotary kiln. Raw materials is heated and decomposed to produce clinker, which contains chunks of non-combustible materials. The clinker flows into coolers from kiln head at about 1,000°C. The clinker cooler is a typical mobile refrigeration equipment, which cold air is pushed in.

All the cement manufacturing process can provide the high-temperature conditions to produce clinker. Which process is adopted depends on the operation conditions and fuel efficiency.

3.1.2.1 Dry process

In the dry process, raw materials are dried and milled to powder, and enters the preheater or precalciner. In rare conditions, raw materials directly flow into rotary kiln to increase the energy efficiency.

To avoid energy waste, a preheater tower including a series of cyclones is installed before rotary kiln. Raw materials enter the tower from the top and the high-temperature flue gas flows in opposite direction with raw materials from the bottom to preheat raw materials. Raw materials are separated with flue gas in the preheater and enter the rotary kiln, which is shorter than that without preheater because of higher temperature of raw materials.

Alkali bypass system is needed in preheater to remove some unnecessary compositions, such as alkali. The alkali compositions can be enriched in rotary kiln and make it difficult to clean the sediments on the surface of rotary kiln, even needing to stop the cement production. Pumping part of flue gas containing high concentration of alkali can help solve the problem. If another stack is built by the alkali bypass system, the flue gas emitted is the same as the flue gas of rotary kiln.

Like the preheater process, the precalciner process before the rotary kiln can increase the temperature of raw materials. The flame tube of precalciner is connected to the bottom of the preheater. The precalciner can also increase the production capacity of rotary kiln. The life length of rotary kiln is extended by the lower heat load of combustion area. However, this process makes it necessary to install an alkali bypass system to control the alkali concentration in flue gas. If all the flue gas is emitted from a stack, the compositions are the same as the flue gas in the rotary kiln.
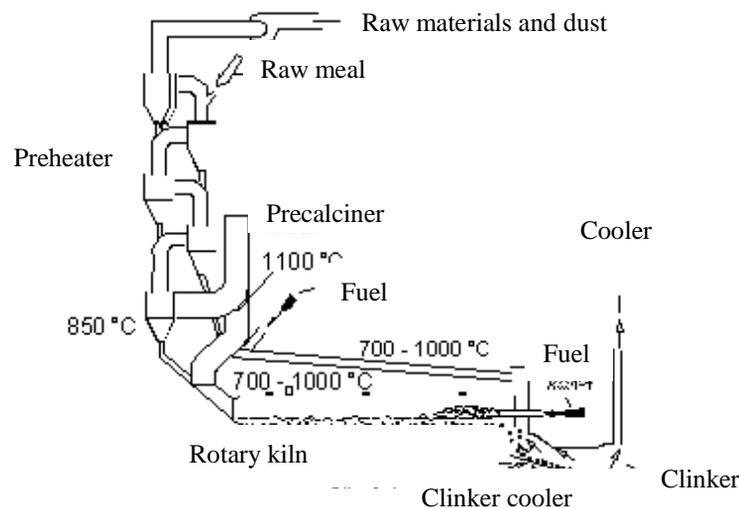

Figure 3-1   rotary kiln with preheater and precalciner

3.1.2.2 Semidry process

In the semidry process, the raw meal is composed of dry raw materials and 12-14% water by weight. The raw meal enters the preheater or long rotary kiln with a cross, dried by the high-temperature flue gas and calcined.

3.1.2.3 Semi-wet process

In the semi-wet process, the raw materials, generally having a high percentage of water, is milled in water to produce slurry. Then the slurry is dehydrated in filter press to make small raw material balls. The raw material balls enter the preheater or directly flow into rotary kiln to produce clinker.

3.1.2.4 Wet process

In the wet process, the raw materials, generally having a high percentage of water, is milled in water to produce slurry. Then the slurry is directly transmitted to rotary kilns or preheater. The wet process is a conventional process, which is usually used for milling raw materials in water. Since the water vaporization needs more energy, the wet process has higher energy consumption.

3.1.3 Air pollution control devices

The particular matter is the predominant pollutant for air pollution control of cement manufacturing process in China. Currently ESPs and FFs are often installed in cement plants. More than 90% of cement plants in China have installed ESPs and FFs.

Desulfurization devices are not generally installed in cement plants. However, in some plants with a high sulfur concentration in raw materials, wet scrubber is used.

The NOx removal technologies in cement plants are predominantly preliminary synthetic method, including flame cooler, boiler design, staged combustion or SNCR.

3.2 Atmospheric mercury emissions in cement manufacturing process

The raw materials used in cement production include limestone, clay, iron-containing materials, coal powder, sandstone and slag. Oil, natural gas, garbage, Petroleum coke, waste solvent, and waste solvent are also used in some plants. It is found that trace mercury exists in all the materials, and is emitted to the flue gas in high-temperature manufacturing process. The mercury concentration in limestone

ranges largely 0.001-2mg/kg, and has a larger variance of 0.002-3.25mg/kg in clay. The variance makes it difficult to accurately estimate the mercury emissions of cement plants.

Part of the mercury in the flue gas is collected by the dust collectors and other facilities, and enters the solid materials. The other part is emitted into the atmosphere. The mercury in the solid materials has a different output because of the different flow of solid materials. When the solid materials are recycled into the rotary kiln, mercury is also cycled in the cement manufacturing process, and the outputs of the whole process include clinker and flue gas. The mercury concentration in clinker is usually quite low and thus the preliminary output for mercury in raw materials and fuel is the flue gas. When part of the solid materials, such as collected dust is disposed out of the manufacturing process, the mercury is therefore also emitted through solid materials and the mercury emission to atmosphere is reduced. Since the heavy metals are concentrated in fly ashes, the fly ashes should be disposed carefully and usually recycled.

The atmospheric emissions of cement plants are usually estimated using emission factor. 65-100 mg Hg/t cement is often used in previous studies(Pacyna and Pacyna，2002; Pacyna et al.，2006; Pacyna et al.，2010). And 40mg Hg/t cement is also used in some studies to avoid the duplicate calculation of coal contribution(Streets et al.，2005; Wu et al.，2006). Some other studies indicate that the mercury emission factor of cement plants is approximately 26-34 mg Hg/t clinker(Lee，2012). Obviously there is a large uncertainty in emission factor of cement plants.

Currently there is a lack of studies on the mercury behavior and emissions in cement manufacturing process, and the mercury concentration in raw materials.

3.3 The best environmental practices to control mercury emissions from cement manufacturing process

The best environmental practices to control mercury emissions from cement manufacturing process include:

- Identify key process parameters, either from site-specific investigations or research undertaken on similar facilities elsewhere;

- Introduce measures that enable control of key process parameters;

- Introduce monitoring and reporting protocols for key process parameters;

- Introduce and follow planning cycles, implement appropriate inspection and maintenance cycles;

- Introduce an environmental management system that clearly defines responsibilities at all levels;

- Ensure adequate resources are available to implement and continue best environmental practices;

- Introduce process improvements to reduce technical bottlenecks and delays;

- Ensure all staff are appropriately trained in the application of the best environmental practices relevant to their duties;

- Define a fuel specification for key fuel parameters and introduce a monitoring and reporting protocol;

3.4 Mercury control technologies for cement plants

Control of mercury emissions for cement plants mainly focus on the precalciner process and presented as follows.

3.4.1 Mercury input reduction

The mercury emissions in cement manufacturing process are mainly from rotary kiln, and depend on the mercury input from raw materials. Therefore, reducing the mercury input can contribute a lot for atmospheric emission reduction. The reduction of mercury input includes choosing the raw materials and fuel with low mercury concentration, and taking some measures to reduce the mercury concentration in raw materials and fuel.

3.4.1.1 Coal washing

Generally speaking, mercury mainly exists in the inorganic minerals. Mercury can be concentrated in the waste residue and separated with the raw materials when washing. A recent study indicates that mercury and inorganic elements are closely interdependent. Mercury may mainly exist in sulfide combination or residual state, and is enriched in pyrite. According to tests of 26 bituminous coal samples by the U.S. environmental protection agency in 2001, the mercury efficiency is between 3% ~ 64%, and the average is about 30% for coal washing. In addition to the conventional method of coal washing, mercury can further be removed by the method of elective sintering, pillar type foam flotation. The latter has been practiced commercially. Some test results show that combined with the conventional washing method, the mercury

removal efficiency is 40% ~ 82%. Coal washing can be a means of mercury removal for power plants, but is not true for cement production. Most of the mercury in the cement manufacturing process is from raw materials. Besides, the wastewater treatment cost is very high. Therefore the contribution of coal washing for mercury control of cement plants is limited.

3.4.1.2 Fuel choosing

In addition to the traditional fuel, other fuel such as tyre derivatives fuel (TDF) can contribute to the mercury reduction because of its low mercury content. A test on a 55 kW pilot boiler indicated that the use of TDF significantly affected the mercury speciation in flue gas, and increased the proportion of oxidized mercury. This may be caused by the high Cl content. Oxidized mercury can be easily removed by the air pollution control facilities. The contribution of fuel with low mercury concentration is limited by the proportion of mercury input from fuel in cement manufacturing process.

3.4.1.3 Raw materials washing

The raw material washing basically includes cleaning and gasification. Cleaning method refers to separate mercury with raw materials through water cleaning because of the water-soluble oxidized mercury. Gasification means that the mercury in raw materials is vaporized through heating and consequently adsorbed by the activated carbon tower. The cost of raw materials washing is quite high considering the large amount of raw materials used in the cement manufacturing process. Therefore, washing of raw materials is generally not appropriate for mercury emission control of cement plants.

3.4.2 Synergetic mercury removal of APCDs

Since the mercury cycles as discussed above largely depend on the removal efficiencies of dust collectors, especially the FFs, the mercury removal efficiency of heating fly ashes can be promoted by a high mercury enrichment and removal efficiency of different facilities. Theoretically the method of fly ash disposal and recycle to reduce mercury enrichment all comply with the above description. Therefore the enhancement of mercury removal of present air pollution devices is significantly crucial for the mercury emission control of the cement manufacturing process with or without dust recycle.

3.4.2.1 Mercury removal of ESPs

The dust removal efficiency of ESPs is generally over 99%, thus the particle-bound mercury is removed simultaneously. However, other mercury species cannot be largely removed.

3.4.2.2 Mercury removal of FFs

Since mercury can be concentrated on the fine particles, FFs have a higher mercury removal efficiency than ESPs. The higher removal efficiency is contributed by that not only particle-bound mercury but also other gaseous mercury are removed by FFs. The longer contact time between gaseous mercury and dust cake are considered to be the main reasons. The different dust removal mechanism of FFs and larger contact area also contribute to the higher mercury removal efficiency. The comparison of mercury removal efficiencies for ESPs and FFs indicates that the removal efficiency of ESPs is 4-20%, while it is 20-80% for FFs.

3.4.3 Reducing the mercury enrichment

The collected dust is mixed with raw materials and enters the rotary kiln to produce clinker in precalciner process. Therefore, the mercury removed by dust collectors is cycled to the kiln system and increase the mercury concentration in raw meal, and the mercury concentration in flue gas emitted from rotary kiln. The mercury concentration in dust is higher than that in raw materials. If dust is not added into the raw materials, the mercury input will largely decrease. However, the large amount of dust can still cause some other problems.

Another method is to add the dust which is heated to remove mercury to raw materials and recycle to rotary kiln. This method can reduce the mercury enrichment and avoid disposing the large amount of dust. Currently a technology of roasting process has been invented and applied for a patent. The test results indicate that the mercury amount in collected dust by FFs can take about 60% of total mercury input for rotary kiln. The fly ashes can be regarded as a good absorbent. The dust is first heated by a heat source, such as the flue gas emitted from rotary kiln, to vaporize mercury and then enters the cycle. The vaporized mercury can be separated with the dust through an ESP under the high temperature. The collected dust is recycled to raw meal silo and mixed with raw materials to produce clinker. The flue gas through the ESP is cooled down and the mercury can be adsorbed by the remaining dust and added sorbents. A FF after the ESP can remove the dust in the flue gas. The collected

dust can be added in the cement or disposed as waste. The heat air and amount of sorbent are estimated to be smaller than the activated carbon inject system. The above technology is still in development, and thus the removal efficiency and cost is not very clear. Because of the high mercury removal efficiency of ESP, the amount of sorbents to adsorb gaseous mercury is also not clear(Zheng et al., 2012).
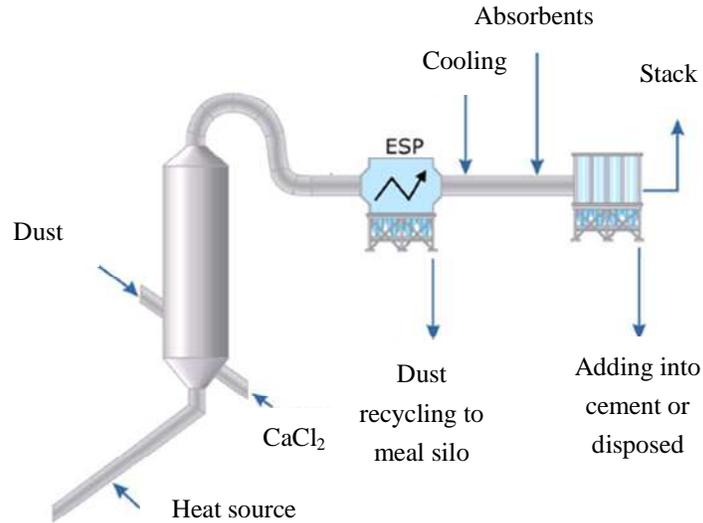

Figure 3-2　Dust calcination system

3.4.4　Mercury removal technologies

If the mercury input reduction is difficult, the synergetic removal efficiency is low because of the mercury cycles, and reducing the mercury enrichment is also not enough to meet the mercury emission standard, some special mercury removal technologies can be adopted before the stack.
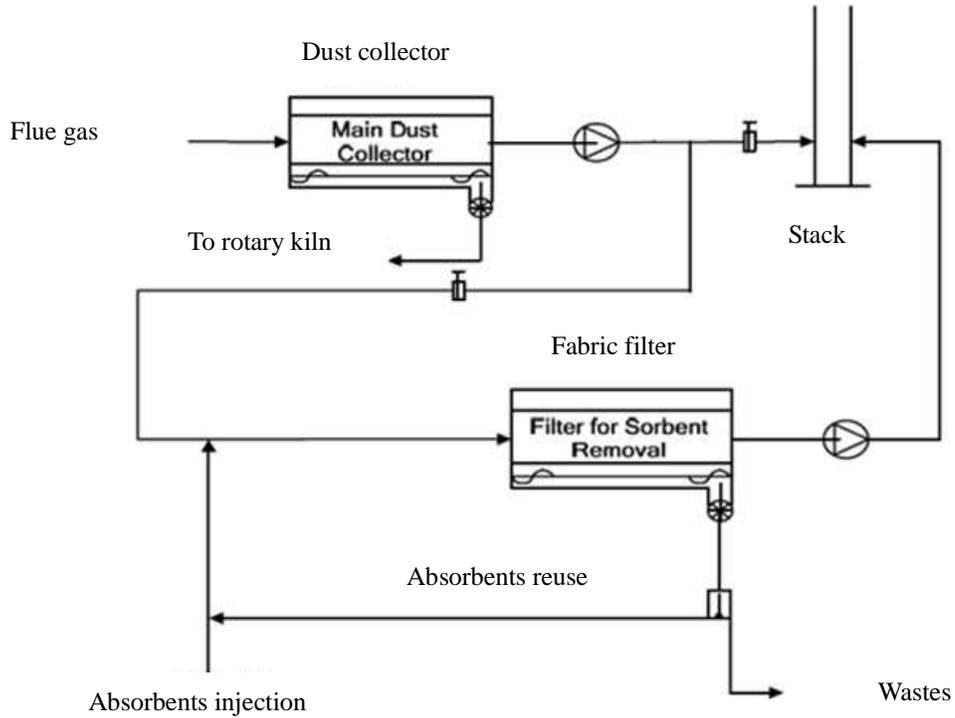
3.4.4.1 Activated carbon injection

Figure 3-3   a schematic diagram of activated carbon injection

The three activated carbon injection (ACI) technologies widely used in power plants include injection before dust collector, after flue gas cooling down, and after dust collector with another extra dust collector added. The activated carbon (AC) suspends for 1-3 seconds in flue gas, and then removed by FFs. ESPs are not appropriate because of the mercury desorption.

The factor influencing the mercury removal efficiency of ACI include mercury concentration and speciation, physical and chemical characterization of AC, size distribution, pore structure and distribution, surface characterization, temperature and compositions of flue gas, AC concentration, contact time between AC and mercury, and the dispersion of AC in flue gas.

The mercury adsorption capacity on AC is related with mercury speciation under a constant temperature. The AC has a stronger adsorption ability for $HgCl_2$ than Hg. Other studies also indicate that the adsorption ability for elementary mercury of S-AC is also enhanced. In real flue gas, the existing HCl in flue gas can transform elementary mercury into oxidized mercury, and therefore, there is no significant

difference between the adsorption of elementary mercury and oxidized mercury.

The mercury adsorption on AC is significantly influenced by the temperature of flue gas. A lower temperature will help increase the adsorption of mercury. The removal efficiency ranges 10-70% at 170℃, while 90-99% at 100℃. Generally speaking, the high-temperature flue gas at the kiln tail cools down rapidly after flowing through heat recovery boiler. The temperature for mercury adsorption is crucial for ACI technology.

The humidity of flue gas is also an important factor. A humidity of 5-10% can largely affect the mercury capture because of the inhibition of water.

The adsorption is significantly affected by acid gas in flue gas. The addition of HCl and NOx has been confirmed to enhance the mercury capture of AC.

The cost of ACI is quite high. For a production line of 1 million tons/year, the construction cost can reach 20 million dollars and the operation cost is 4 million dollars. Besides, the disposal of AC after adsorption is difficult. Therefore, ACI technology is rarely applied in cement plants. There is only one reported cement plant in German adopting ACI.

3.4.4.2　Activated carbon bed

The flue gas flows through an adsorption bed in activated carbon bed technology, and the principles are similar with the activated carbon injection. The adsorption equilibrium is important in activated carbon adsorption. The activated carbon reaching equilibrium should be replaced and treated to remove adsorbed mercury or just disposed as waste. However, because of the concentrated heavy metals, the activated carbon should be regarded as hazardous waste. The cost of this technology is quite high. The short life and blocking also increase the operation cost. Currently there is only one facility installed in Europe. Activated coke is similar with activated carbon with a high cost, these technologies are not appropriate for commercial use.

3.4.4.3　Wet scrubber

When the flue gas flows through spray tower in opposite direction with limestone slurry, SO_2 is adsorbed to form $CaSO_3$ and oxidized to $CaSO_4$. Because of the lower temperature, mercury, especially $HgCl_2$ is collected in slurry.

Multiple pollutants, such as SO_2 and other acid gas, can be removed using wet scrubber and absorbents injection. Mercury can be removed with waste water and gypsum through wet scrubber. In United States, wet scrubbers are installed in some

cement plants. Though these scrubbers are mainly for SO_2 control, mercury is also removed.

Wet scrubbers have some limitations. The crystallization of gypsum can be affected by dust. Therefore, the wet scrubber should be installed after the dust collector. More energy is consumed because of the use of big fans. The water consumption is also large. The low concentration of SO_2 can cause a small production amount of gypsum and low mercury removal efficiency. The mercury speciation is crucial for the removal efficiency since only oxidized mercury can be removed.
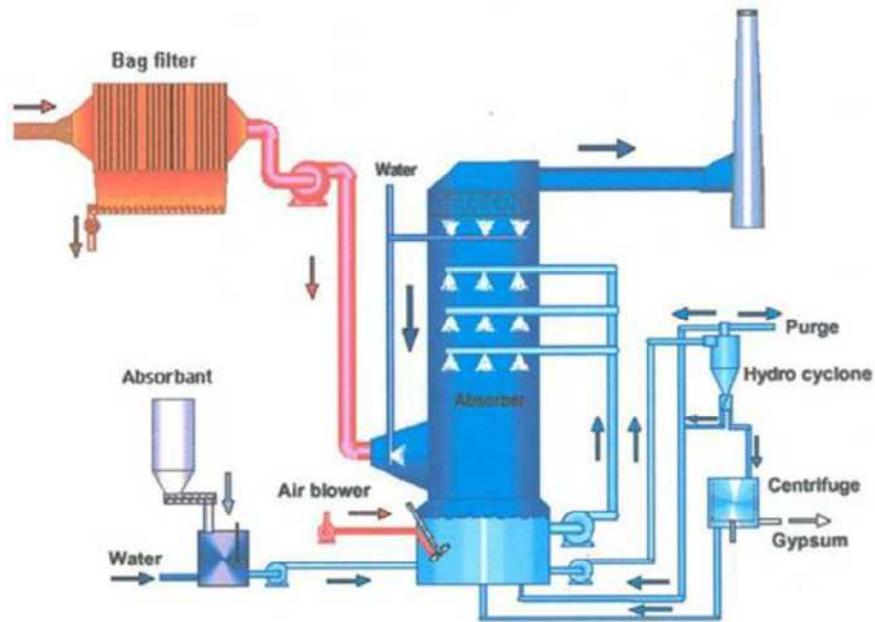

Figure 3-4   a schematic diagram of wet scrubber

3.4.4.4 Dry/semidry scrubber

Acid gas and mercury is adsorbed in a reactor filled with absorbents in dry scrubber. This technology is widely used in power plants, and some cement plants. Other suspended absorbers remove acid gas and mercury through the contact between flue gas and absorbents. The used absorbents are partly recycled, and disposed as waste. The dry scrubber should be installed after dust collector. The mercury removal efficiency can reach 80-90% in some studies. Compared with the wet scrubber, the effects of mercury speciation have smaller effects on Hg removal efficiencies of dry scrubber. The removal efficiency is higher than activated carbon injection because of the temperature control in suspended absorber. The energy consumption of

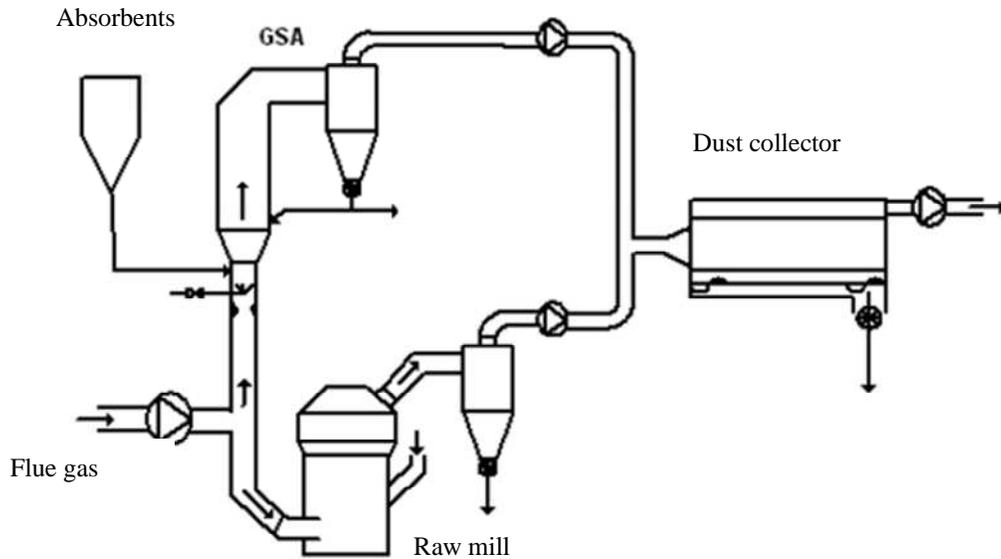dry/semidry scrubber is smaller than wet scrubber, but larger than activated carbon injection technology.

Figure 3-5   a schematic diagram of dry scrubber

3.5   Mercury emission standard of Chinese cement plants

Only the emission concentration of conventional air pollutants are listed in the current Cement industry air pollutants emission standards(GB4915-2004). Mercury is not included in this emission standard.

According to the newly released Cement industry air pollutants emission standards(GB4915-2004), the mercury emission standard is 0.05 mg/m^3 for the new cement plants built after March 1st 2014, and for the existing plants from July 1st 2015.

The mercury emission standard is regulated as 0.05 mg/m^3 in Cement plant design specifications(GB 50295—2008), when waste is synergistically disposed. The mercury concentration in cement should be lower than 0.5 mg/kg.

The mercury concentration should be lower than 0.05 mg/m^3 in the flue gas of kiln and heat recovery system when solid waste is synergistically disposed in cement kilns after March 1st 2014, according to Standard for pollution control on co-processing of solid wastes in Cement kiln (GB 30485—2013).

4 Waste incinerators

Incineration is used as a treatment for a very wide range of wastes. The objective of waste incineration is to treat wastes so as to reduce their volume and hazard, whilst capturing (and thus concentrating) or destroying potentially harmful substances that are, or may be, released during incineration. Incineration processes can also provide a means to enable recovery of the energy, mineral or chemical content from waste.

4.1 Process

Incinerators come in a variety of furnace types and sizes as well as combinations of pre- and post-combustion treatment.

Incinerators are usually designed for full oxidative combustion over a general temperature range of 850 °C – 1,400 °C. This may include temperatures at which calcinations and melting may also occur.

Waste is generally a highly heterogeneous material, consisting essentially of organic substances, minerals, metals and water. During incineration, flue gases are created that will contain the majority of the available fuel energy as heat. In fully oxidative incineration the main constituents of the flue gas are water vapour, nitrogen, carbon dioxide and oxygen. Depending on the composition of the material incinerated , operating conditions and the flue gas cleaning system installed, acid gases (sulphur oxides, nitrogen oxides, hydrogen chloride), particulate matter (including particle-bound metals), and a wide range of volatile organic compounds, as well as volatile metals (such as mercury) are emitted. Formation is normally substantially increased in units that are poorly designed or operated.

Depending on the combustion temperatures during the main stages of incineration, mercury in the input wastes is totally or partly evaporated to the flue gas. A mineral residue fly ash (dust) and heavier solid ash (bottom ash) are created. Figure 4-1 presents a simplified flow scheme of an incinerator.
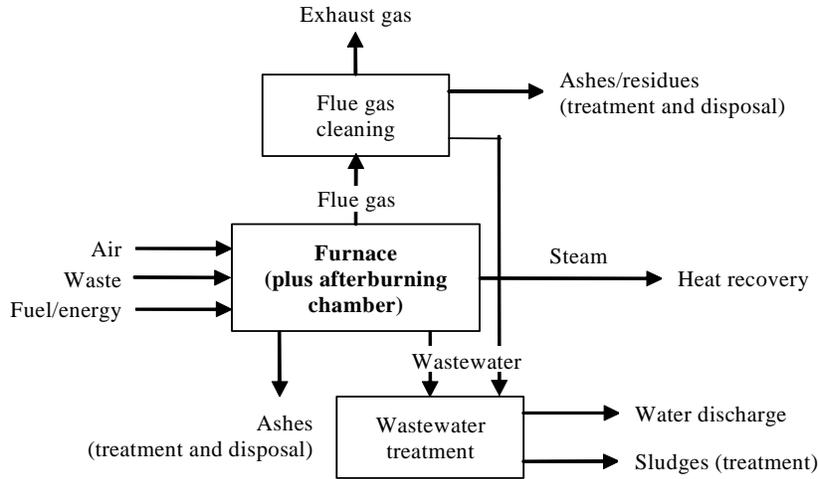
Figure 4-1 Simplified flow scheme of an incinerator

4.1.1 Municipal solid waste incineration

Municipal solid waste incineration is commonly accompanied by the recovery of some energy ("waste to energy") in the form of steam and/or the generation of electricity. Incinerators can also be designed to accommodate processed forms of municipal solid waste derived fuels, as well as co-firing with fossil fuels. Municipal waste incinerators can range in size from small package units processing single batches of only a few tons per day to very large units with continuous daily feed capacities in excess of a thousand tons.

By the end of 2010, there have been 170 municipal solid waste incinerators in China, accounting for 20% of the managed waste. Since generally there are no mercury recovery facilities, the mercury-containing wastes, including fluorescent lamps, thermometers, pressure gages, and batteries, introduce mercury into the municipal solid wastes.

The process for municipal solid waste incineration has been commercialized for many years in China. Usually these waste incinerators install both advanced semi-dry flue gas cleaning system and bag house, which ensures the emissions lower than the standard.

4.1.2 Hazardous waste incineration

Incineration and other forms of thermal treatment also represent options for the treatment of hazardous waste. Mercury in the hazardous wastes is mainly from the

used mercury-containing products and industrial wastes.

Similar to the incineration of municipal solid waste, hazardous waste incineration offers the benefits of destruction of organic (including toxic) materials, of volume reduction and concentration of pollutants into relatively small quantities of ashes, and, less frequently, energy recovery.

The most common combustion technology in hazardous waste incineration is the rotary kiln, but grate incinerators (including co-firing with other wastes) are also sometimes applied to solid wastes, and fluidized bed incinerators to some pretreated materials. Static furnaces are also widely applied at on-site facilities at chemical plants.

In a rotary kiln solid, sludge, containerized or pumpable waste is introduced at the upper end of the inclined drum. Temperatures in the kiln usually range between 850 °C (500 °C when used as a gasifier) and 1,450 °C (as a high-temperature ash melting kiln). Almost all mercury in the solid waste was released to the flue gas.

Most hazardous waste incinerators are modernized and installed with quenching tower, semi-dry type reactor; lime and activated carbon are added in front of the semi-dry flue gas cleaning system and bag house, which ensures the emissions lower than the standard.

4.1.3 Domestic sewage sludge

The incineration of sewage sludge is practiced in many countries, either alone or through co-incineration in municipal solid waste incinerators or in other combustion plants (e.g. coal-fired power plants, cement kilns). Similar to the municipal solid waste and hazardous waste, the sewage sludge also contains mercury which is emitted to flue gas after incineration.

A typical sewage sludge incinerator may process as much as 80,000 tons of sewage sludge (35% dry solids) per year. The incineration technologies of choice for sewage sludge are the multiple hearth and fluidized bed furnace systems, although rotary kilns are also used in smaller applications.

Sewage sludge is co-incinerated with municipal solid waste in both fluidized bed and mass burn (grated) incinerators. In the latter case, a ratio of 1:3 (sludge to waste) is typical, with dried sludge introduced into the incineration chamber as a dust or drained sludge applied to the grate through sprinklers.

4.1.4　Medical waste incineration

Certain amounts of medical waste are produced in hospitals. Incineration of medical waste is performed in order to reduce the volume of waste. Most medical waste does not contain mercury and will not emit mercury, except for mercurial thermometer and blood pressure gauge.

4.2 BEP

Mercury emissions from municipal and medical waste incinerators may be reduced by separating the small fraction of mercury containing waste before it is combusted. However, separation programmes are sometimes difficult or costly to implement widely, especially when dealing with the general public. In such cases a better long-term solution may be to strongly encourage the substitution of non-mercury products for those containing mercury.

4.3 Technologies to control mercury emissions from incinerators

The PM control devices most frequently used are electrostatic precipitators (ESPs) and fabric filters (FF), which both remove particulate mercury. Wet scrubbers also remove oxidized mercury in the flue gas.

Typically, municipal waste combustion systems use a combination of gas cooling and duct sorbent injection (DSI) or spray dryer (SD) systems upstream of the particle removal device to reduce temperatures and provide a mechanism for acid gas control.

4.3.1　Duct sorbent injection (DSI)

Mercury emissions from medical and municipal waste incineration can be controlled relatively well by addition of a carbon sorbent. Duct sorbent injection has been widely used in the waste incinerators in Europe and United States. The most common sorbent is PAC. The sorbent is usually injected before the existing PM control equipment and can be captured by the following PM control equipment.

Such control technology can have 90% Hg removal efficiency.

4.3.2　Semi-dry spray tower and CFB-FGD

Semi-dry spray tower and CFB-FGD are the most widely used flue gas cleaning equipment in Chinese municipal waste incinerators. These technologies not only meet the requirement of emission standards, but also have the advantage of no waste water

and low cost (Cui et al., 2007).

4.3.2.1 Semi-dry spray tower

Semi-dry spray tower system consists of spray dryer tower, limestone slurry system, activated carbon injection, and fabric filter. Limestone slurry is introduced into a spray dryer tower. A high-speed centrifugal nozzle is installed at the top of the tower, which atomized and injected the 9-13% limestone slurry into flue gas. Very fine droplets are commonly generated.

Flue gas from waste incinerator enters into the top of the tower. The acid gases (e.g., HCl, SOx and HF, etc.) react with the limestone slurry and precipitate to the bottom of the tower with larger particles in the flue gas. Activated carbon is injected into the duct after the tower, which removes dioxins as well as mercury in the flue gas.

A waste incinerator in Shenzhen introduced Seghers flue gas purification technology, which uses rotating spray semi-dry flue gas cleaning system. This flue gas treatment unit can remove multi-pollutant in the flue gas, including dust, SOx, NOx, heavy metals, dioxins and other pollutants. The mercury removal efficiency reaches nearly 90% (Li, 2006; Cui et al., 2007).

4.3.2.2 CFB-FGD

CFB-FGD technology has been applied in coal-fired and waste-to-energy plants. CFB-FGD technology has the advantages of removing multi-pollutants including SO_2 and mercury, fewer moving parts resulting in high availability and lower maintenance cost. CFB-FGD has a mercury removal efficiency of over 90% (Lin, 2008).

4.4 Mercury emission standard for waste incinerators in China

In 2001, Chinese government released the Pollution Control Standard for Municipal Waste Incineration (GB 18485-2001) and Pollution Control Standard for Hazardous Waste Incineration (GB 18484-2001).

These standards set up the threshold value for mercury emissions from municipal waste incineration and hazardous waste incineration as 0.2 mg/m^3 and 0.1 mg/m^3, respectively. With advanced technologies, most newly built waste incinerators in China can meet the standards.

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