能源与环境出版工程

总主编　翁史烈

Coal Fired Flue Gas Mercury Emission Controls

燃煤烟气汞排放控制（英文版）

Jiang Wu　Yan Cao　Weiguo Pan　Weiping Pan

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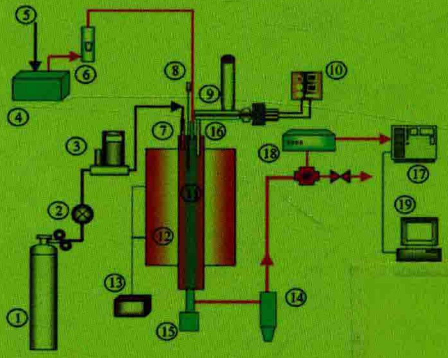

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内容提要

汞对环境和人类健康造成严重危害，其排放控制日益引起重视。本书对自然和人为汞排放，特别是燃煤电站汞的形态转化、迁移特性及其影响因素进行了系统论述；全面介绍了汞排放的控制方法，如电厂现有空气污染控制设备对烟气汞的脱除、吸附剂喷射技术等。本书系统地给出了实验室、中试以及工业应用规模上吸附剂喷射的实验研究成果，将有助于研究人员和工程师对吸附剂喷射法降低汞排放机理的理解以及应用这些方法在燃煤发电厂进行汞排放的控制。通过阅读本书，读者可以全面地了解烟气汞排放控制方法及其工业应用。

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能源与环境出版工程

总　　序

能源是经济社会发展的基础，同时也是影响经济社会发展的主要因素。为了满足经济社会发展的需要，进入21世纪以来，短短十年间(2002—2012年)，全世界一次能源总消费从96亿吨油当量增加到125亿吨油当量，能源资源供需矛盾和生态环境恶化问题日益突显。

在此期间，改革开放政策的实施极大地解放了我国的社会生产力，我国国内生产总值从10万亿元人民币猛增到52万亿元人民币，一跃成为仅次于美国的世界第二大经济体，经济社会发展取得了举世瞩目的成绩！

为了支持经济社会的高速发展，我国能源生产和消费也有惊人的进步和变化，此期间全世界一次能源的消费增量28.8亿吨油当量竟有57.7%发生在中国！经济发展面临着能源供应和环境保护的双重巨大压力。

目前，为了人类社会的可持续发展，世界能源发展已进入新一轮战略调整期，发达国家和新兴国家纷纷制定能源发展战略。战略重点在于：提高化石能源开采和利用率；大力开发可再生能源；最大限度地减少有害物质和温室气体排放，从而实现能源生产和消费的高效、低碳、清洁发展。对高速发展中的我国而言，能源问题的求解直接关系到现代化建设进程，能源已成为中国可持续发展的关键！因此，我们更有必要以加快转变能源发展方式为主线，以增强自主创新能力为着力点，规划能源新技术的研发和应用。

在国家重视和政策激励之下，我国能源领域的新概念、新技术、新成果不断涌现；上海交通大学出版社出版的江泽民学长著作《中国能源问题研究》(2008年)更是从战略的高度为我国指出了能源可持续的健康发展之路。为了“对接国家能源可持续发展战略，构建适应世界能源科学技术发展趋势的能源科研交流平台”，我们策划、组织编写了这套“能源与环境出版工程”丛书，其目的在于：

一是系统总结几十年来机械动力中能源利用和环境保护的新技术新成果；

二是引进、翻译一些关于“能源与环境”研究领域前沿的书籍，为我国能源与环境领域的技术攻关提供智力参考；

三是优化能源与环境专业教材，为高水平技术人员的培养提供一套系统、全面的教科书或教学参考书，满足人才培养对教材的迫切需求；

四是构建一个适应世界能源科学技术发展趋势的能源科研交流平台。

该学术丛书以能源和环境的关系为主线，重点围绕机械过程中的能源转换和利用过程以及这些过程中产生的环境污染治理问题，主要涵盖能源与动力、生物质能、燃料电池、太阳能、风能、智能电网、能源材料、大气污染与气候变化等专业方向，汇集能源与环境领域的关键性技术和成果，注重理论与实践的结合，注重经典性与前瞻性的结合。图书分为译著、专著、教材和工具书等几个模块，其内容包括能源与环境领域内专家们最先进的理论方法和技术成果，也包括能源与环境工程一线的理论和实践。如钟芳源等撰写的《燃气轮机设计》是经典性与前瞻性相统一的工程力作；黄震等撰写的《机动车可吸入颗粒物排放与城市大气污染》和王如竹等撰写的《绿色建筑能源系统》是依托国家重大科研项目的新成果新技术。

为确保这套“能源与环境”丛书具有高品质和重大社会价值，出版社邀请了杜祥琬院士、黄震教授、王如竹教授等专家，组建了学术

指导委员会和编委会，并召开了多次编撰研讨会，商谈丛书框架，精选书目，落实作者。

该学术丛书在策划之初，就受到了国际科技出版集团 Springer 和国际学术出版集团 John Wiley & Sons 的关注，与我们签订了合作出版框架协议。经过严格的同行评审，Springer 首批购买了《低铂燃料电池技术》(*Low Platinum Fuel Cell Technologies*)，《生物质水热氧化法生产高附加值化工产品》(*Hydrothermal Conversion of Biomass into Chemicals*)和《燃煤烟气汞排放控制》(*Coal Fired Flue Gas Mercury Emission Controls*)三本书的英文版权，John Wiley & Sons 购买了《除湿剂超声波再生技术》(*Ultrasonic Technology for Desiccant Regeneration*)的英文版权。这些著作的成功输出体现了图书较高的学术水平和良好的品质。

希望这套书的出版能够有益于能源与环境领域里人才的培养，有益于能源与环境领域的技术创新，为我国能源与环境的科研成果提供一个展示的平台，引领国内外前沿学术交流和创新并推动平台的国际化发展！

翁史烈

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Preface

Mercury (Hg) is considered as a global pollutant and is one of the most toxic heavy metals commonly found in the global environment including lithosphere, hydrosphere, atmosphere and biosphere, which has a long residence time in the atmosphere from 0.5 to 2 years. Coal combustion, waste incineration, metal mining, refining and manufacturing and chlorine-alkali production are currently major anthropogenic source categories in the industrialized world.

Coal-fired power plants have been considered to be the primary anthropogenic source of mercury into the atmosphere. After inhalation of Hg by human beings, elemental Hg vapor rapidly diffuses through the alveolar membrane and is absorbed through the lungs, and has a bad effect on the nervous system, particularly with regard to early-life neurodevelopment. Therefore, the research on mercury in America and Europe has been widely conducted. Anthropogenic emissions of mercury still increase in Asia because of increased burning of coal and increased industrialization.

During coal combustion at a coal-fired power plant, the mercury (Hg) in coal is volatilized and converted to elemental mercury (Hg^0) vapor in the high temperature regions of coal-fired boilers. As the flue gas is cooled, a series of complex reactions begin to convert Hg^0 to oxidized mercury (Hg^{2+}) compounds and/or Hg compounds (Hg_p) that are in a solid-phase at flue gas cleaning temperatures or Hg that is adsorbed onto the surface of other particles. Coal Fired Derived Flue Gas Mercury Measurement mainly includes Ontario Hydro Method (OHM), Semi-Continuous Emission Monitor (Hg-SCEM) and Appendix K. The comparison between different mercury emission measurement methods have been investigated in detail in this book.

The authors have investigated the effect of halogen on mercury speciation; Cl_2, HCl, and HBr gases were injected in the slipstream reactor by the control of a mass flow controller (MFC). HI and HF were injected using HI and HF solutions. Moreover, the constituents of flue gas including SO_x, NO_x, O_2, H_2O and fly ash have been certified to play an important role in mercury reactions in flue gases from coal combustion in air.

A cost-effective mercury emission control technology is required to reduce the global emission of mercury. Oxidized mercury can be removed in the wet flue gas desulfurization (WFGD) facilities of coal combustion processes, and particle-bound mercury can be captured along with fly ash in electrostatic precipitators (ESP) or baghouses. Due to Hg^0 being difficult to control for its insolubility in water, the mercury control technologies are to convert or transfer Hg^0 into oxidized mercury or particle-bounded mercury, which are easier to be controlled by existing APCDs at coal-fired power stations. By comparison, the direct oxidation method of injecting a type of oxidant, such as modified activated carbon, fly ash and some novel sorbents, into flue gas to oxidize Hg^0 appeared to be a simpler method.

In this book, the authors set up a lab-scale multiphase flow reactor and a pilot-scale slipstream reactor and conducted such evaluation on the two scales. After that, some kinds of sorbents were injected at a full-scale power station. The experimental results show that the lab- and pilot-scale reactor systems can provide accurate information of sorbent evaluation under flue gas atmosphere. SO_2 in the flue gas was shown to inhibit mercury oxidization and capture. The sorbents have higher mercury capturing efficiency with higher injection rate and longer residence time when other conditions were held constant. In the pilot-scale, four injection ports vertical to the flue gas flow direction could help improve mixture of sorbent and flue gas so that the mercury removal efficiency became higher. The pilot-scale data can be used to predict the full-scale results. Some of the chemical and physical mechanisms responsible for the mercury removal of the sorbents were identified.

We also have designed a pilot-scale coal-combustion furnace and constructed to study the mercury speciation and transformations in the flue gas under different conditions. Its purpose was to study the effect of chlorine compounds on mercury speciation and transformation. The addition of chloride additive makes the percentage of both gaseous bivalent and gaseous elemental mercury in the total mercury decline at some degree, and percentage of particle mercury increase correspondingly. However, with the increase in additives, the increasing trend of particle mercury became flat gradually and the decreasing of elemental mercury becomes gentle gradually.

Another effective method is the oxidation of elemental mercury with oxidants such as HCl or Cl_2 or ozone over a catalyst followed by the removal of oxidized mercury (Hg^{2+}) with scrubber solution in the WFGD facilities. The extent of Hg^0 oxidation is affected by the presence of coexisting gases such as NH_3, NO, SO_2 and concentration of the oxidant (HCl). Most mercury control technologies have been developed and tested on conventional pulverized coal (pc)-fired power plants. In the next decade, mercury emissions control will be improved on the basis of the existing technologies, which include fuel/raw material pretreatment, existing air pollution control devices (APCDs), mercury adsorption, and mercury oxidation.

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Contents

Chapter 1
Mercury and Its Effects on Environment and Human's Health

Abstract Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment including the lithosphere, hydrosphere, atmosphere, and biosphere. Hg is released to the atmosphere from natural and anthropogenic sources. Coal combustion, waste incineration, metal mining, refining and manufacturing, and chlorine-alkali production are currently major anthropogenic source categories in the industrialized world.

It was estimated that approximately 33 % of these anthropogenic sources are coal-fired combustion sources. Mercury (Hg) is considered as a global pollutant because Hg^0 is the predominant form of atmospheric Hg, which has a long residence time in the atmosphere from 0.5 to 2 years. After inhalation of Hg by human beings, elemental Hg vapor rapidly diffuses through the alveolar membrane and is absorbed through the lungs. While there is a considerable body of experimental evidence on the reproductive effects of organic mercury at relatively low exposures, the available human evidence is restricted to a few limited studies reporting fluctuations in fertility and sex ratio in relatively highly exposed groups such as residents of Minamata City in Japan. Thus, as noted by, it is considered that the nervous system should still be the critical endpoint of concern, particularly with regard to early life neurodevelopment.

Keywords Mercury • Emission sources • Mercury speciation and transportation • Environment • Health

1.1 Mercury Emission Sources

Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment including the lithosphere, hydrosphere, atmosphere, and biosphere. A series of complex chemical transformations allows the three-oxidation states of Hg to cycle in the environment [1]. Most of the Hg encountered in all environmental media (water/soil/sediments/biota) is in the form of inorganic mercuric salts and organo-mercurics, with the sole exception of atmosphere. The mercuric salts $HgCl_2$, $Hg(OH)_2$, and HgS are the prevalent forms existing in the environment, and CH_3HgCl and CH_3HgOH are main forms of organic compounds, together with

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other organo-mercurics (i.e., dimethylmercury and phenylmercury) existing in small fractions. Natural, anthropogenic, and reemitted sources are the three major sources of Hg emissions [2].

The linear correlations among mercury concentration in soil and mercury concentration in different tissues of corn plant are studied. It is showed that mercury concentration in root tissue of corn plant is most significantly correlated with mercury concentration in soil with a correlation coefficient of 0.716 ($p < 0.01$), demonstrating that mercury in root tissue may be mainly derived from soil. Mercury concentration in leaf tissue correlated significantly with that in root tissue and soil, which does not necessary imply that mercury in leaf is derived from soil and root pathway.

Total mercury concentrations in corn grain tissue were the lowest in all tissues of the corn plant, but the average concentration reached 0.011 mg/kg, which is close to the Chinese guidance limit for foodstuff other than fish that is 0.02 mg/kg. It is observed that mercury concentration in grain tissue of one sample collected at TQ14 reached 0.026 mg/kg, exceeding the national guidance limit for foodstuff other than fish.

Hg is released to the atmosphere from natural and anthropogenic sources [3]. Coal combustion, waste incineration, metal mining, refining and manufacturing, and chlorine-alkali production are currently major anthropogenic source categories in the industrialized world. Human activities emit both elemental Hg (Hg^0) with a long life in the atmosphere and reactive gaseous mercury (RGM) and particulate Hg, which are short lived in the air and deposited near the emission source [4].

Mercury is also released into the atmosphere by a number of natural processes, including volcanoes and geothermal activities [5], evasion from surficial soils, water bodies, vegetation surfaces, wild fires, as well as the reemission of deposited mercury [6]. Mercury released from natural sources is believed to be mainly Hg^0.

In 1997, the EPA issued a Mercury Study Report to Congress, which estimated that anthropogenic sources in the USA emitted 158 tons of mercury into the atmosphere in 1994–1995. The report estimates that approximately 33 % of these anthropogenic sources are coal-fired combustion sources [7]. Because of the danger to human health posed by mercury, Congress and the EPA are determined to regulate mercury emissions. The EPA has set a target date of 2004 for new mercury regulations. At the same time that the EPA seeks to lower total mercury emissions, there is a resurgence in the construction of new coal boilers. Therefore, the need to control and measure mercury emissions in a cost-effective manner has become an issue of importance to both the coal industry and regulators.

Mercury emissions are regarded as one of the most problematic environmental issues in the world because of their propensity toward bioaccumulation within an aquatic food chain [8]. After bioaccumulation, mercury may result in neuron damage to humans.

Hg emissions from coal-fired power plants contribute about 30 % to the anthropogenic sources of mercury. Coal contains naturally occurring mercury that varies with both the coal rank and its origin. Mercury (Hg) is a ubiquitous, persistent, and toxic environmental pollutant. Once released to the environment, elemental mercury can be converted in aqueous media into the highly toxic methyl mercury, which is accumulated efficiently in the aquatic food chain. It becomes concentrated in top vertebrates, for example, in predatory fish, birds, and mammals, where it poses a risk for wild life and humans. Mercury enters the terrestrial and aquatic biosphere mostly by wet and dry deposition of atmospheric mercury species, which are operationally defined as gaseous elemental mercury (GEM), gaseous ionic mercury called reactive gaseous mercury (RGM) , and mercury associated with aerosols, designated particulate mercury (Hg_p). The three atmospheric mercury species have grossly different physical and chemical properties: the lifetime is short (days to weeks) for RGM and pHg; the lifetime of GEM is much longer (e.g., 1 year), but spatially variable [9]. Distant from point sources, GEM accounts for >95 % of the total atmospheric mercury, with concentrations less than 1 part per trillion by volume [ppt(v)].

1.2 Mercury Speciation and Its Transportation

When elemental mercury enters soil, it may undergo several transformations depending on soil characteristics. Some elemental mercury will likely volatilize and enter the gaseous phase. Gaseous mercury may be lost from the system, but some will likely be adsorbed onto the surface of soil particles. The behavior of the mercury that remains in soil will initially be governed by physical and chemical processes, redistributing the mercury within the soil and allowing some of the mercury to enter solution. Once in solution, adsorption–desorption reactions will initially dominate [10]. Subsequently, the mercury can undergo volatilization or biological or chemical transformations [11]. The final equilibrium forms of mercury will depend upon the organic matter quantity and quality, soil texture and mineralogy, and the chemistry of the soil solution [12].

Mercury (Hg) is considered as a global pollutant, because Hg^0 is the predominant form of atmospheric Hg, which has a long residence time in the atmosphere from 0.5 to 2 years. It can be transported and deposited to remote places even 1,000 km away from the sources [6]. Furthermore, Hg can be converted to methylmercury (MeHg) and accumulated in the food chain, posing a potential threat to humans' health. The concern of Hg pollution arises from the health effects caused by MeHg through the consumption of fish and marine products.

Atmospheric Hg originates from three main sources: anthropogenic sources (e.g., fossil fuel combustion and waste incineration), natural sources (e.g., volcanoes and ocean vents), and reemission of anthropogenic and natural mercury previously deposited onto terrestrial and water surfaces [13]. Long-range transport of GEM, its conversion to RGM and Hg_p, and deposition of these species along a trajectory have caused widespread contamination of aquatic and terrestrial ecosystems, even to those located far from industrial or natural sources.