学校编码：10384　　分类号_____　　密级_____

学号：200434018　　UDC_____

厦门大学

博 士 学 位 论 文

海水脱硫电站燃煤过程中汞的形态转化与排放特性研究

Study on Species Transformation and Emission Characteristic for Mercury during Coal Combustion in Power Station with Sea Water Flue Gas De-Sulphurization

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论文提交日期：2007 年 11 月

论文答辩时间：2007 年 12 月

学位授予日期：2007 年　　月

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2007 年 11 月

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摘 要

汞是一种剧毒、高挥发性、易在生物体内富集并导致病变的持久性环境污染物。由于原煤中含有汞，耗煤量巨大的燃煤电站成为环境中汞污染的最主要人为排放源。目前，燃煤电站汞排放特性及控制技术研究已成为各国研究的前沿及热点。

本文以燃煤过程产生的汞污染物为对象，以配有完整烟气净化装置的大型滨海电站燃煤锅炉烟气的排放流程为主线，研究燃煤过程汞的形态转化与排放特性，结合锅炉燃煤烟气净化工艺，讨论汞污染的控制技术。主要内容和结果如下：

(1) 论文研究了燃煤电站常用的烟煤中汞的含量，分析汞含量与煤种的相关性，发现煤中汞含量与硫含量具有较强的相关性。本研究采用小型管式炉进行燃煤排放烟气中汞的形态分布模拟实验。在 600℃的燃烧条件下，实验煤种汞的析出率大于 95%。模拟实验还发现，烟气中二价汞(Hg^{2+})所占的比例随燃烧温度、燃烧供气流量的增加而上升；零价汞(Hg^{0})所占的比例则随燃烧温度、燃烧供气流量的增加而下降。

(2) 本研究采用 Ontario-Hydro Method (OH 法)，在 300 MW 工业燃煤锅炉进行烟气中汞的浓度水平分析，同时取样分析锅炉的煤、底渣、飞灰等固体样品，以及脱硫塔进出口、曝气池之后海水样品中的汞含量。研究发现，电站燃煤排放烟气中气态汞的浓度在 12.63~15.71 μg/Nm^3 之间变动，飞灰中的汞含量与煤中的汞含量大体相当，底渣中的汞含量则仅为飞灰含汞量的 1/10~1/100 左右。脱硫曝气池的海水在排向海域前的汞含量仍为新鲜海水的 5~6 倍左右。经物料衡算，单位发电量产生的汞源强约为 62.40 μg/kW·h，实测数据计算结果表明，单位发电量排向大气环境的汞约 13.78 μg/kW·h，以灰渣形式排向环境的汞约 3.53 μg/kW·h，排向海水环境的汞约 33 μg/kW·h。

(3) 本研究利用了 OH 法的分析数据以及对飞灰粒径和残碳量的测试结果，并采用连续在线测汞仪(CEMs)监测不同运行工况下烟气中汞的排放浓度变化趋势，同时结合烟气净化设施(FCDs)的工艺特点，分析 FCDs 工艺及运行方式对汞排放特性的影响。研究发现：在选择性催化还原(SCR)脱硝催化剂的

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作用下，烟气中 83.4%的气态 Hg^0 被氧化成气态 Hg^{2+}，强烈地影响汞的后续排放特性。作为 SCR 工艺中的还原剂，NH_3 不会对烟气中汞的形态变化造成可视性(discernable)的影响。烟气经过静电除尘(ESP)的脱尘作用后，颗粒态汞在烟气总汞中所占的比例由 ESP 前的 5.66%降至 ESP 后的近似于零，静电除尘对颗粒态汞的去除率几乎达到 100%。ESP 各电场飞灰吸附汞能力与飞灰粒径呈负相关性，与飞灰残碳量有较强的正相关性。采用烟气海水(SW-FGD)脱硫装置时，海水对烟气中汞的洗脱率高达 73.6%，海水转移了本应排向大气的汞污染物。本研究中 SCR+ESP+SW-FGD 的 FCDs 组合方式对烟气中汞的脱除率达 74.1%。因此认为，烟气净化设施能有效地削减燃煤过程汞的向大气的排放量，有必要充分利用现有烟气净化设施优先控制燃煤锅炉烟气中汞向大气的排放。

(4) 本研究采用金丝捕汞法富集脱硫海水曝气池逸出的汞，考察脱硫海水曝气工艺对汞向大气释放的影响。曝气池上空气体中汞的浓度平均值为 10.01 ng/m^3，高出当地背景值的 20 倍以上。汞的浓度还与曝气池海水中汞的质量浓度、曝气强度呈正相关性。研究还发现，汞的浓度在曝气池周边的垂直高度上呈现递减的规律。曝气池上空汞的浓度在白昼时段高于夜间时段，并在中午日光照射较强的时段出现峰值，光致还原对曝气池海水中的汞释放起到了促进作用。

(5) 本研究建立了三维水动力数学模型，采用具有二次精度的六节点三角形单元，并利用粗细网格共存及多套网格一次剖分的非结构化网格技术，模拟和预测脱硫海水中汞在附近海域的排放规律，通过对排水口附近海域海水中汞含量的实地监测，验证预测模型的准确性。

关键词：汞；燃煤锅炉；烟气；汞的形态分析；烟气净化设施；海水脱硫曝气工艺；数学模型；排放趋势预测.

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ABSTRACT

Mercury has been identified as a persistent pollutant with characteristics of high toxicity, volatility, bioaccumulation and mutagenicity to human health and environment. Since the coal contains mercury, the coal-fired power plants have become the main source for anthropogenic discharge of mercury to the atmosphere. The emission features and the control of mercury exhausted from coal-fired power plants are currently an active topic and highlight interest of research.

This research chose the mercury emitted from coal combustion as the objective, investigated the exhaust process of flue gas from the large-scale industrial boiler equipped with flue gas cleaning devices (FCDs) in the power plant near sea, and focused on the mercury species transformation and emission characteristic during coal-firing. Based on the study results, the mercury control measures are also discussed. The detail information is as follows:

(1) The mercury contents in bituminous coals were analyzed. It is observed that the mercury contents had a positive correlation with the sulphur contents in coal. A small-scale tube-furnace was assemblied for simulating mercury species transformation in flue gas. The result showed that the release percentage of mercury from coal was higher than 95% under 600℃ combustion temperature. The content of Hg^{2+} in the flue gas increased with the increase of combustion temperature and air flow rate, while Hg^0 decreased with the increase of the combustion temperature and air flow rate.

(2) Ontario-Hydro (OH) method had been applied to determine the mercury concentrations and species in the flue gas emitted from a 300 MW coal-fired boiler. Mercury concentrations in raw coal, bottom ash and fly ash of the boiler, seawater at the inlet and outlet of SO_2 absorption reactor and the drainage of aeration sink were also analyzed. The results indicated the concentrations of mercury in flue gas ranged from 12.63 μg/Nm^3 to 15.71 μg/Nm^3, the mercury content in fly ash was close to that in coal, while in bottom ash was only about 1%~10% of that in fly ash. The mercury concentration in the seawater of aeration sink drainage was 5~6 times higher than that in fresh seawater. The calculation from materiel equilibrium showed that the mercury produced by a unit of electric-power generation was

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62.40 μg/kW·h, and the field experimental data revealed that the amounts of mercury exhausted to atmosphere, remained in fly ash and bottom ash, discharged into seawater for flue gas de-sulphurization (FGD) were 13.78, 3.53, 33 μg/kW·h, respectively.

(3) The data of OH experiment, the analysis of remnant carbon contents and sizes distribution of particulate in fly ash, and the concentration variety of mercury in flue gas supervised by an on-line continuous emission monitor (CEMs) were employed to further study the effects of FCDs on mercury emission from coal-fired boiler. It is found that Selective Catalytic Reduction (SCR) De-NOx device had strong impact on the mercury species transformation, and the conversion rate of Hg^0 to Hg^{2+} by the catalyst was as high as 83.4%. As the reducing reagent in SCR technology, NH_3 had no discernable effect on the concentration and species of mercury in the flue gas. After passing through the electrostatic precipitator (ESP), particulate mercury in the flue gas dropped from 5.66% of the total amount at the inlet of the ESP to zero at the outlet, and the removal efficiency of particulate mercury by the ESP was almost 100%. The amounts of mercury in the fly ash in the hoppers of the ESP had a negative correlation with the particulate sizes, on the other hand, showed a positive correlation with the remnant carbon contents in the fly ash. With seawater flue gas de-sulphurization (SW-FGD), the removal efficiency of mercury was as high as 73.6%. The amount of mercury that could have been exhausted into the atmosphere if without the SW-FGD, however, was discharged into the seawater. The total removal of mercury by FCDs combined with SCR+ESP+SW-FGD reached 74.1%. The study showed that FCDs in coal-fired power plant play an important role on mercury emission, which is feasible to be applied for cutting down the amounts of mercury discharged into the atmosphere.

(4) The method of gold amalgamation was employed to determine the concentration of total gaseous mercury (TGM) in the air above the aeration sink for the SW-FGD, and mercury concentration in the seawater of the sink was also analyzed for evaluating the effect of aeration technology on the amount of mercury released. The results showed that the average concentration of TGM was about 10.01 ng/m^3, which was 20 times higher than that of local background. The concentrations of TGM above the aeration sink presented a positive correlation with mercury concentrations in seawater of the FGD and aeration intensity. The

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experiment also found that the TGM concentrations decreased as the vertical height near the aeration sink increased, and the TGM concentrations above the aeration sink in daytime, especially during noon time, were higher than those at night, which could be explained by the photo-reduction of mercury.

(5) In order to evaluate the discharge of mercury from sea water of the FGD into the sea areas nearby, a three dimensional hydrodynamic numerical model with 6-node triangular element and two order shape function were developed. The model simulated and predicted the concentration distribution of mercury from seawater of the FGD into the sea. The field study was also carried out for verifying the model.

Keywords: Mercury, Coal-fired boiler, Flue gas, Mercury species analysis, Flue gas cleaning devices, Aeration technology of seawater FGD, Numerical model, Drainage trend predication.

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