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直接碳燃料电池(DCFC)实验研究

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摘 要:直接碳燃料电池是一种高效、清洁的燃料电池技术,其原理是碳和氧气勿需气化和重整而直接通过电化学反应产生电能,效率可达80%,燃料利用率约达100%。自行组装了DCFC单体电池,工作温度为500~700 ℃;该电池采用熔融氢氧化物作电解质,并掺入一定量的催化剂;石墨作阳极,不锈钢作阴极,加湿氧气作氧化剂。对不同的电解质、不同的氧气流量下DCFC的输出性能进行了试验研究。结果表明,KOH比NaOH的导电性好,电池运行更稳定,更有利于电池的输出;氧气流量为70 mL/min时,该电池的输出性能最佳,最大电流密度、功率密度分别为105 mA/cm^{2}和0.041 W/cm^2,开路电压达到0.74 V。电流密度为45 mA/cm^{2}时,输出电压0.65 V,可连续稳定运行20 h。提出了热解-直接碳燃料电池联合系统,并以$C_{10}H_{22}$为例,分析了联合系统发电效率高达76.5%,表明该系统在未来集中式电厂中有很好的应用前景。

关 键 词:直接碳燃料电池;石墨;熔融氢氧化物;开路电压

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引 言

作为燃料电池的一种,直接碳燃料电池(DCFC)原理为碳(碳的衍生物)和氧气经过电化学反应直接产生电能,不必进行气化;具有转化效率高、清洁、燃料适应性广的特点。直接碳燃料电池工作温度400~1 000 ℃,可以采用石墨、活性炭、煤焦炭、生物质焦炭等为燃料[1~3]。

直接碳燃料电池采用碳为燃料的优点:(1)与其它燃料电池相比,DCFC采用碳为燃料,每升氧气氧化碳会放出更多的能量20.0 kWh/L,而氢气为2.4 kWh/L,甲烷为4.2 kWh/L[3];(2)由反应$C+O_2 \rightarrow CO_2$可知,在标准状态下,该反应的熵变(ΔS)接近零;焓变与吉布斯自由能的变化几乎相等,故DCFC理论效率可达100%,实际运行效率达80%;(3)电池反应生成气体仅是CO_2,便于回收[3~5]。

1 直接碳燃料电池

1.1 单体直接碳燃料电池

Jacques于1896年提出了DCFC的概念和电池原型[1],Tao在工作温度1 000 ℃下使用熔融碳酸盐作电解质[2],DCFC最大功率密度约为10 mW/cm^2。Cherepy N J等人对DCFC阳极材料进行了优化[3],以焦炭、无烟煤、活性炭等为阳极材料、熔融碳酸盐混合物为电解质,800 ℃下DCFC最大电流密度约为150 mA/cm^2,最大功率密度为84 mW/cm^2。但DCFC的发展受到阳极反应速率低、电解质易变质、缺乏适合的阴极材料、功率密度和电流密度低等问题的困扰进展比较缓慢[2~5]。

为提高DCFC的功率密度和电流密度,对单体直接碳燃料电池进行了组装、研究。DCFC单体燃料电池如图1所示,电池外壳材料为SSL316不锈钢,不锈钢外壳同时充当电池的阴极,该材料具有较强的耐酸碱、耐腐蚀性能,采用机械加工成型。熔融氢氧化物为电解质,并掺入一定量的催化剂;燃料采用石墨,石墨具有导电性,在电池中同时是阳极,石墨阳极产生的电流由Pt丝引出,通过导线与电流、电压检测仪相连。不锈钢外壳阴极由导线与电流、电压检测仪相连。氧气在加湿后,经不锈钢管进气口通入到电解质内。

与熔融碳酸盐电解质相比,采用熔融氢氧化物电解质具有如下优点:(1)具有更高的电导性和较低的超电势[5~6];(2)熔点较低(450~750 ℃),降低了电池的运行温度,从而降低了电解质对阴极的腐蚀,允许用廉价的不锈钢做阴极;(3)温度越低,越有利于CO_2的生成,抑制CO的生成,本电池采用500 ℃为工作温度,降低了CO_2向CO的转化[5]。

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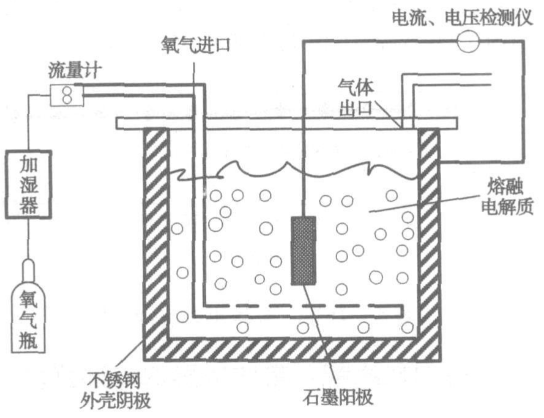

图 1　单体直接碳燃料电池

熔融氢氧化物电解质存在的问题是, 由于生成的CO_2会和电解质发生反应生成碳酸盐, 反应为:

$$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O$$

根据化学反应平衡原理可知, 增大生成物浓度, 可以使反应向逆向进行。本实验通过对氧气加湿, 增大了电解质中水分含量, 减少氢氧化物向碳酸盐的转化。

1.2　熔融氢氧化物电池电极反应

由于氧化程度不同, C 可能被氧化成 CO_2 或 CO[3], 因此熔融氢氧化物电解质中阳极碳氧化规律还不明确, 根据 J. F Cooper 在熔融碳酸盐电解质电池中提出的碳氧化规律[4~5], 得出阳极反应:

$$6OH^- \rightarrow 3O^{2-} + 3H_2O \tag{1}$$

$$C + 3O^{2-} \rightarrow CO_3^{2-} + 4e^- \tag{2}$$

$$C + 6OH^- \rightarrow CO_3^{2-} + 3H_2O \uparrow + 4e^- \tag{3}$$

$$C + 2CO_3^{2-} \rightarrow 3CO_2 \uparrow + 4e^- \tag{4}$$

根据 Andrew L. Dicks 的研究[5], 在熔融氢氧化物电解质中, 氧气大部分还原生成超氧离子(O_2^-), 其余部分直接还原为氧离子; 氧还原过程由以下反应组成:

$$O_2 + e^- \rightarrow O_2^- \tag{5}$$

$$O^{2-} + 3e^- + 2H_2O \rightarrow 4OH^- \tag{6}$$

$$2O_2 + 4e^- \rightarrow 2O^{2-} \tag{7}$$

$$2O^{2-} + 2H_2O \rightarrow 4OH^- \tag{8}$$

从而得出阴极反应[5~6]:

$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \tag{9}$$

因此, 电池总反应为:

$$C + O_2 \rightarrow CO_2 \tag{10}$$

2　实验部分

实验中采用的石墨阳极(燃料)是河北生华石墨厂提供, 自行加工体积为 2.2 cm^3。以内径 3.2 cm、高 12 cm 的不锈钢管(SSL316)作阴极; 氢氧化钠、钾(分析纯, 天津化学试剂三厂)为电解质; 氧化剂为加湿氧气。电池内部参数如表 1 所示。

表 1　电池参数

工作温度/ ℃	电解质/ cm^3	阳极长/ cm	阳极宽/ cm	阳极高/ cm	阳极面积/ cm^2
500	80	3.5	0.8	0.8	12

按图 1 组装成电池, 以石墨作阳极, 不锈钢作阴极; 以 NaOH 为电解质, 掺入一定量的催化剂。电池组装完后, 维持一定的组装压力, 将电池启动升温, 电解质加热熔化, 温度达到 500 ℃时, 氧气通过恒温水浴后以一定的流量通入到电池内部, 并由流量计控制流量。电池开始反应, 通过电流、电压检测仪观察电池的输出性能。

3　结果分析及研究

3.1　电流电压及电池功率特性

图 2 给出了工作温度 500 ℃, 氧气流量为 70 mL/min 时, DCFC 单体电池输出电流与电压、功率之间的关系。由图可知, 电池电压随着电流密度的增大而减小, 而功率密度随着电流密度的增大先增大后减小, 当电流密度为 86 mA/ cm^2 时, 功率密度出现最大值 0.041 W/ cm^2。这是因为, 随着电池运行时间的增大, 电池阴阳极间的电势差随着氧化程度的提高而减小; 从而导致电池输出电压的减小。

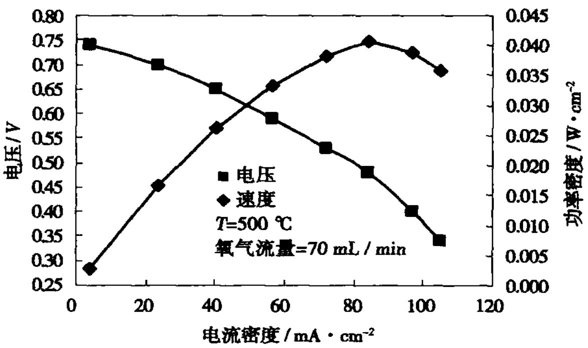

图 2　电池输出 *I-V-ρ* 图

3.2　氧气流量对电池性能影响

阴极侧氧气的操作条件对电池性能影响很大。氧气浓度增加, 提高了氧离子传质速度, 会明显提高电池性能。实验采用了 3 种不同的氧气流量, 对电

池性能进行测试,结果如图 3 所示。随着电流密度的增大,低氧气流量电池性能下降更为明显。在电流密度为 60 mA/cm^2 时,25 mL/min 氧气流量相比 70 mL/min 流量时,电池电压下降 0.5 V。高氧气流量可以提高阴极反应速度,但流量太大时,会加快阴极氧化腐蚀,反而不利于氧气的还原[4]。该电池适宜的氧气流量为 25 ~ 100 mL/min。

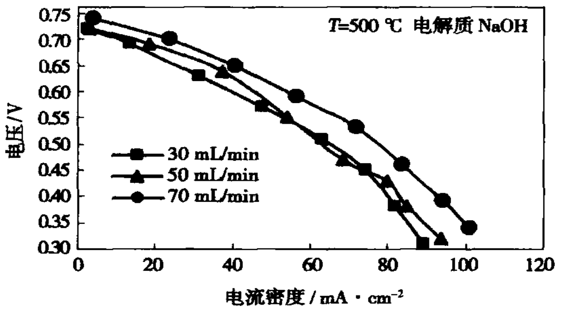

图 3 不同氧气流量下,电池输出 *I-V* 图

3.3 熔融电解质对电池性能的影响

图4 给出了工作温度 500 ℃,氧气流量为 50 mL/min,电解质 NaOH 以及 NaOH ∶KOH (质量比=1∶1)时,电池输出性能的对比情况。从图中可以看出,电解质中添加 KOH 后,电池的开路电压、电流密度都明显增大,输出更加稳定。在电流密度为 60 mA/cm^{2}时,相对 NaOH,添加 KOH 后,电池电压增大 0.3 V。在电解质 KOH 中,氧气可以大部分还原成超氧离子,提高了阴极反应速度[5],降低了电池的内阻,提高了电池的输出性能。

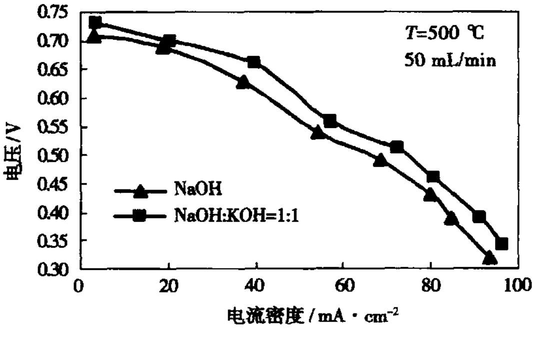

图4 不同电解质下,电池输出 *I-V* 图

3.4 电池稳定性

考察了单体 DCFC 以 NaOH 为电解质,氧气流量为 70 mL/min 时,电池在 500 ℃下的运行稳定性。图5 给出电流密度为 45 mA/cm^2 时,电池稳定输出电压为 0.65 V,连续运行了 20 h 。结果表明,DCFC 单体电池在 500 ℃下工作时,可以稳定输出功率密度 0.033 W/cm^2,工作电流密度 45 mA/cm^2。

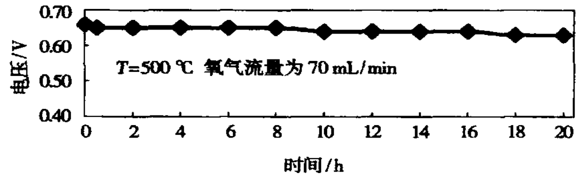

图 5 DCFC 单体电池稳定性

4 含碳燃料热解—直接碳燃料电池联合发电系统

目前,含碳燃料(生物质、煤、燃油等)热解气化是制可燃气的普遍路线,尤其是生物质热解技术。生物质热解产物中含有将近 20%(质量分数)的焦炭,传统技术都是将焦炭再燃,利用率很低。直接碳燃料电池是以碳为燃料新型燃料电池,其实际发电效率可达 80%,与碳再燃技术相比,很大程度上提高了碳的利用率。将直接碳燃料电池系统与生物质热解系统、固体氧化物燃料电池系统构成联合发电系统,宜适用于大规模集中式电厂[3,7~8]。

4.1 热解及燃料电池联合系统

生物质热解可采用流化床热解系统,生物质颗粒可用高纯氮气输送,热解后冷凝,经旋风分离器将 C 与热解气分开。热解气中含有大量的 N_2 和 CO_2,可经过净气系统回收 N_2 和 CO_2,则尾气中含有高热值的可燃气(H_2、CO、CH_4)。固体碳颗粒可送入直接碳燃料电池系统,用于发电,生成的 CO_2 可回收利用。可燃气可送入固体氧化物燃料电池(SOFC)系统用于发电,整个系统如图 6 所示。

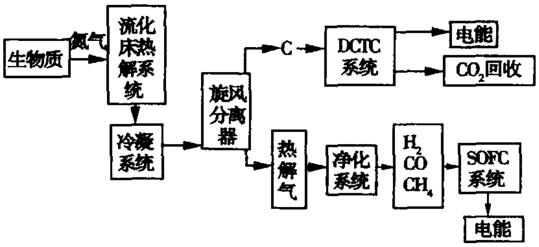

图 6 热解/DCFC 联合系统流程图

4.2 联合系统效率分析

如图7 所示,以 $C_{10}H_{22}$(煤油主要成分)为例,其高、低位发热量分别为 6 752 kJ/mol、6 268 kJ/mol。针对上述系统,分析联合系统效率 η。假定热解过

程消耗的能量约为 $C_{10}H_{22}$ 高位发热量的 3％。1 mol $C_{10}H_{22}$ 经热解后生成 10 mol C 和 11 mol H_2, 将生成的 10 mol C 送入 DCFC 系统, DCFC 发电效率为 80％, 可得到 3 163. 10 kJ 电能。11 mol H_2 送入 SOFC 系统, SOFC 发电效率为 50％[8], 得到电能 1 429. 21 kJ; 尾气中的氢气和水蒸气经后置燃烧室后由凝汽器冷却变成液态水。将整个系统总能量与 $C_{10}H_{22}$ 的低位发热量相比, 可得出该联合系统发电效率 η 高达 76. 5％, 与煤气化-固体氧化物燃料电池混合系统效率(60％多)相比有很大的提高[8], 表明该系统在未来高效、可持续发展的电力供应中具有很好的应用前景。

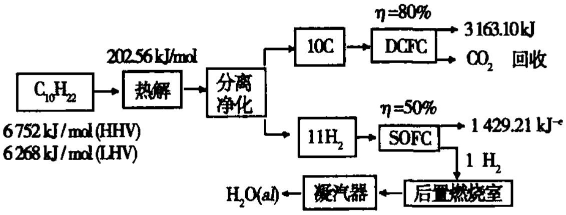

图 7　联合系统实例流程图

5　结　论

（1）成功设计、组装了 DCFC 单体电池, 电解质配比, 电池电流、电压检测均为自行研制。

（2）氧气流量对电池性能影响很大, 随着氧气流量的增大, 电池性能有很大提高, 但是为了减少阴极的氧化腐蚀, 氧气流量应控制在合适的范围之内（25 ~ 100 mL/min）。

（3）电解质 KOH 比 NaOH 具有更好的电导性, 电池运行更稳定, 有利于电池的输出。

（4）以石墨为燃料的 DCFC 单体电池, 工作温度 500 ℃, 电流密度 45 mA/cm^2 时, 输出电压 0. 65 V, 可连续运行 20 h, 性能非常稳定。电池开路电压可达 0. 74 V, 最大电流密度、功率密度分别为 105 mA/cm^2 和 0. 041 W/cm^2。

（5）将直接碳燃料电池系统与流化床热解系统、固体氧化物燃料电池系统组成联合系统, 并以实例分析了联合系统的发电效率, 得出效率高达 76. 5％; 表明该联合系统在未来大规模集中式电厂中有很好的应用前景。

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6　结　论

（1）CO 余热锅炉经改造后提高了再生烟气处理能力, 解决了过热器容易超温的问题, 提高了热效率并降低了排烟温度。

（2）催化裂化装置能耗降低了 29.3×10^4 kJ/t。

（3）每天节约原水 120 t/h, 解决了由于原水杂质多而影响采样器换热效果的问题。

（4）改造后把因余热锅炉炉膛压力高而被迫直排烟囱的 15％CO 再生烟气并入余热锅炉进行余热回收, 避免了 CO 再生烟气直接向烟囱排放, 改善厂区周围环境所带来的社会效益也十分有意义。

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（编辑　何静芳）

基于相空间重构的锅炉炉膛火焰信号分析＝**An Analysis of Flame Signals in a Boiler Furnace Based on a Phase Space Reconstruction**［刊，汉］/MA Shao-hua, HUA Ying（College of Electrical Engineering under the Shenyang Polytechnical University, Shenyang, China, Post Code：110023）, LI Xiao-bai（China National Fire-fighting Electronic Product Quality Supervision and Inspection Center, Shenyang, China, Post Code：110031）//Journal of Engineering for Thermal Energy &Power. －2007, 22(4). －440～442, 456

By employing chaotic and fractal theory, a qualitative analysis and quantitative calcualtion have been conducted of the flame signals measured from a boiler furnace. Through a restructuring of phase spaces, obtained were the time- sequence phase-plane map and correlation dimensions of burning flames under both stable and unstable combustion conditions. The analysis and calculation results indicate that under a stable combustion state, the two-dimensional phase-plane map of the flame signals is relatively wide and their correlation dimensions range from 5.5855 to 6.8415. Under an unstable combustion condition, the two-dimensional phase-plane map of the flame signals is relatively narrow and their correlation dimensions range from 5.8843 to 6.0907. Under both working conditions there exists a conspicuous difference between the flame time- sequence phase-plane map and correlation dimensions. However, the correlation dimensions during stable combustion are always considerably greater than those during unstable combustion. Hence the correlation dimensions can be used as a characteristic parameter to identify the state of flame combustion. The combustion diagnosis method proposed by the authors can provide an effective approach for developing innovative optical-type flame detectors. **Key words**: furnace flame, combustion diagnosis, status discrimination, restructuring of phase spaces, number of correlation dimensions, chaos, fractal science

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CO余热锅炉增设旁通烟道及省煤器技术改造＝**Technical Modification of a CO Heat Recovery Boiler with the Addition of a Bypass Flue Duct and an Economizer**［刊，汉］/YAN bin（China Petroleum Corporation Harbin Petrochemical Subcompany, Harbin, China, Post Code：150056）//Journal of Engineering for Thermal Energy &Power. －2007, 22(4). －443～445, 449

Enumerated were the problems existing in a 1.2 Mt/a RFCCU incineration-type CO heat recovery boiler of Harbin Petrochemical Sub-company affiliated to China Petroleum Corporation. Following a thermal and flue duct resistance calculation, a variety of improvement measures, such as additional provision of a bypass flue duct and an economizer as well as the use of a XD-2000 type gas impulse soot blower, were implemented. They have enhanced the steam output, flue-gas energy recovery capacity and thermal efficiency of the CO heat recovery boiler, thus meeting the demand of a plant exhausting at high loads all the flue gas into the heat recovery boiler. If the current 15％ of regenerative flue gas is exhausted through a bypass, i.e. the flue gas discharge quantity being assessed at 20 000 m^3/h（420 ℃ and CO content 6％）, the thermal energy recovered shall be 21.06×10^6 kJ/h. The energy consumption of a cracking plant can be decreased by 29.3×10^4 kJ/t, equivalent to newly accrued economic benefits of about RMB 8 million yuan per year. This represents a significant energy-saving effectiveness. **Key words**：catalytic cracking plant, CO heat recovery boiler, bypass flue duct, bypass economizer

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直接碳燃料电池（DCFC）实验研究＝**An Experimental Study of Direct Carbon Fuel Cells（DCFC）**［刊，汉］/CHEN Hong-wei, WANG Jin-quan, GAO Jian-qiang, et al（College of Energy Source and Power Engineering under the North China University of Electric Power, Baoding, China, Post Code：071003）//Journal of Engineering for Thermal Energy &Power. －2007, 22(4). －446～449

Direct carbon fuel cells（DCFC）represent an effective and clean fuel-cell technology, which is based on the theory of producing electric energy directly through an electrochemical reaction of carbon and oxygen with no need for gasification and reforming. Its efficiency can be as high as 80％ and fuel utilization rate can reach about 100％. A single-body cell of DCFC was assembled with its working temperature ranging from 500 to 700 ℃. The cell uses fusible hydroxide to serve as an electrolyte with a certain amount of catalyst being added. Graphite is used to serve as a positive pole and stainless steel as a negative one with moistened oxygen being added to serve as an oxidation agent. An experimental study has been performed of the output performance of DCFC by using different electrolytes and at different oxygen flow rates. The results of the study show that KOH has a better conductivity than NaOH and the cell made from KOH can operate more stably and is more favorable for cell output. When the oxygen flow rate is 70 ml/min, the cell has an optimum output performance with its maximal current and power density being 105 mA/cm^2 and 0.041 W/cm^2 respectively. The open-circuit voltage

can reach 0.74 V. When the current density is 45 mA/cm^2, the output voltage can reach 0.65 V and the cell can maintain a continuous and stable operation for 20 hours. A pyrolysis and direct carbon fuel-cell combined system is proposed and with $C_{10}H_{22}$ serving as an example, an analysis was performed of the combined system having a maximal power generation efficiency of 76.5%. This indicates that the system in question will have a brilliant application prospect in future centralized power plants. **Key words**: direct carbon fuel cell, graphite, fusible hydroxide, open-circuit voltage

蜂窝状催化剂脱硝过程数值计算 = Numerical Calculation of a Honeycomb-shaped Catalyst Denitration Process

[刊, 汉]/FAN Hong-mei, ZHONG Zhao-ping, JIN Bao-sheng, et al (College of Energy Source and Environment under the Southeast University, Nanjing, China, Post Code: 210096)//Journal of Engineering for Thermal Energy & Power. —2007, 22(4). —450~456

An analytic study was conducted of the convection, mass transfer and chemical reaction process occurring inside a honeycomb-shaped catalyst and a control equation established for the wall surface areas. Boundary conditions were written out on the basis of the geometrical symmetry and diffusion balance with self-adaptive meshes being generated. A discretization of the control equation was performed by using a finite difference method to seek a solution of NO concentration distribution on wall surfaces. Established was a control equation for the inner areas in the honeycomb-shaped catalyst passage and written out were the boundary conditions on the basis of the geometrical symmetry and diffusion balance. A discretization of the control equation was conducted by using an alternating-direction implicit (ADI) algorithm. Finally, simultaneous equations were set up and a solution was sought. Obtained was an optimum NH_3/NO-ratio-based formula for a given temperature, air-flow velocity and certain denitration efficiency as well as under the condition of an acceptable ammonia leakage rate. A specific-case calculation shows that SCR (selective catalytic reduction) reaction only occurs in a thin layer close to the catalyst wall surface and the others are all dead zones. From the concentration distribution of the NH_3 and NO in a catalyst single hole along the axial direction, it can be shown that the concentration of NH_3 in various sections drops quicker than the concentration of NO, a result mainly caused by NH_3 being oxidized at a high temperature. From the optimum NH_3/NO ratio at a certain NO admission concentration, temperature and air-flow velocity, one can conclude that the most suitable NH_3 gas-feeding flow rate is not equimolar with the amount of NO. **Key words**: honeycomb-shaped catalyst, denitration, numerical calculation

湿法烟气脱硫喷淋塔的实验与反应模型研究 = A Study of Experimental and Reaction Models for the Spray Towers of Wet-method Flue-gas Desulfuration

[刊, 汉]/ZHAO Jian-zhi, JING Bao-sheng, ZHONG Zhao-ping (Education Ministry Key Laboratory on Clean Coal Power Generation and Combustion Technology under the Southeast University, Nanjing, China, Post Code: 210096), SUN Ke-qin (Suyuan Environment Protection Engineering Stock Co. Ltd., Nanjing, China, Post Code: 210024)//Journal of Engineering for Thermal Energy &Power. —2007, 22(4). —457~462

Established was a spray-tower test stand for limestone/gypsum wet-method flue-gas desulfuration. An experimental study was perfomed of the mechanism governing the impact of important operating parameters on the desulfuration efficiency of a spray tower. The test results show that it is possible to raise the desulfuration efficiency by employing the following measures: raising liquid-gas ratio and slurry pH value, lowering the flue gas temperature and its flow speed, reducing SO_2 concentration of the inlet flue gas and performing a forced oxidation. The spray slurry was divided into two existing forms: namely, spray liquid droplets and tower-wall liquid film. Models for them were respectively set up. The desulfuration process of the spray liquid droplets was calculated by using a Gerbec liquid-droplet desulfuration model. The flow of tower-wall liquid film was divided into two states, namely, laminar flow and undulatory laminar flow. A new reaction model for calculating desulfuration in the spray tower has been developed. The calculation results obtained by using the model show that relative to the Gerbec liquid-droplet model, the calculation results of the reaction model under discussion are in better agreement with the experimental data. **Key words**: flue gas desulfuration, spray tower, desulfuration efficiency, tower-wall liquid film, reaction model