文章编号: 1001－2060(2004)03－0234－04

微型鼓泡床中石灰石溶解特性的实验研究

时正海, 赵彩虹, 周屈兰, 惠世恩
(西安交通大学 能源与动力工程学院, 陕西　西安　710049)

摘　要: 实验用钢瓶气体模拟实际烟气, 研究了在微型鼓泡床中反应的 pH 值、温度及浆液中微量的氟离子和氯离子对石灰石溶解速度的影响。根据质量作用定律和阿仑尼乌斯方程提出了石灰石溶解速度的数学公式, 式中各项参数物理意义明确, 可统一描述各工况下石灰石溶解速度。同时测出了该实验使用的石灰石溶解速度的各参数, 并得出了浆液中微量的氟离子和氯离子均不利于石灰石的溶解。利用本文提出的模型可以比较不同石灰石的活性, 从而针对不同品种的石灰石设计合适的浆池大小, 这对于研究湿法烟气脱硫具有重要意义。

关　键　词: 鼓泡床; 石灰石; 溶解速度
中图分类号: X701.3　　文献标识码: A

1　前　言

石灰石/石膏湿法烟气脱硫工艺是目前世界上应用最广泛、技术最成熟的二氧化硫脱除技术, 约占已安装 FGD 机组容量的 70%[1]。在湿法烟气脱硫(WFGD)中石灰石的溶解是一个重要的速率控制步骤。目前国内外对石灰石和碳酸钙的溶解展开了很多研究, 但是这些研究大部分局限于研究石灰石或碳酸钙在酸性溶液中溶解速度的影响因素, 而且大部分以单颗粒溶解模型为主, 而在实际脱硫系统中, 石灰石浆液和二氧化硫的给入都是连续的, 本文的研究内容主要是通过模拟烟气与石灰石浆液在特定条件下的反应过程, 研究影响石灰石的溶解速度的因素, 并且提出石灰石溶解的统一模型。

2　实验系统

实验所用的石灰石的成分及粒径范围见表 1, 石灰石颗粒的粒径采用马尔文激光粒度仪分析。

表 1　实验所用石灰石的成分及粒径范围

成　分	ω(CaO)	ω(MgO)	ω(Al_2O_3)	ω(Fe_2O_3)	酸不溶物	粒径范围/μm
质量百分比/%	45.53	2.47	0.16	0.13	5.38	18～35

实验装置如图 1 所示。实验用钢瓶气: 氮气、氧气、二氧化碳及二氧化硫模拟实际烟气, 通过调节气瓶减压阀和流量计的开度来控制模拟烟气的成分, 气体经过流量计和前混气瓶混合后, 以鼓泡的形式进入反应瓶与石灰石浆液进行反应, 反应后的气体经过后混气瓶, 净化后排出。反应瓶的温度用恒温水浴控制, pH 值通过自动电位滴定仪控制浆液的补给量来维持; 进出口模拟烟气的成分使用两台烟气分析仪来测量和记录; 石灰石浆液的补给量使用电子天平隔一定的时间自动采集和记录; 通过我们的实验观察发现鼓泡床的传质非常强烈, 所以本实验系统采用鼓泡的形式使模拟烟气与石灰石浆液进行反应, 这样就可以忽略气液相的传质阻力, 集中研究模拟烟气与石灰石浆液的反应动力学。

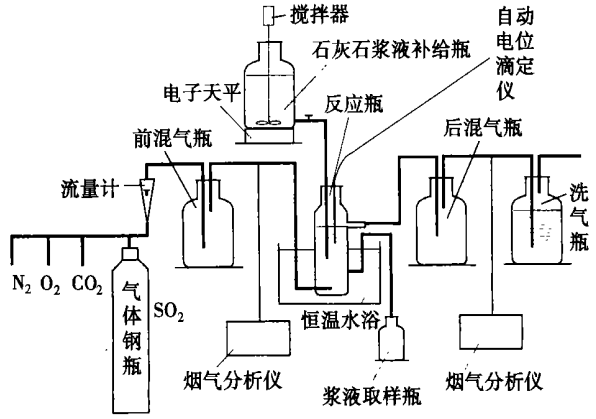

图 1　实验系统图

实验初始时, 调节气相各组分的流量使浓度稳定在要求值, 调节水浴温度使得反应瓶温度达到实验值。此时, 反应瓶的 pH 值还未到设定值, 随着二氧化硫的不断进入, 反应瓶中的 pH 值不断减小, 直至设定值, 此时自动滴定仪开始补给浆液, 当补给浆液量稳定时, 开始记录实验数据。

收稿日期: 2003－06－25;　修订日期: 2003－09－22
基金项目: 国家自然科学基金资助项目(50276051)
作者简介: 时正海(1975－), 男, 江苏东台人, 西安交通大学硕士研究生.

3　实验结果及公式推导

3.1　实验结果

碳酸钙溶解的化学方程式如下：

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2(aq)$$

$$CO_2(aq) \rightleftharpoons CO_2(g)$$

实验所用的石灰石浆液的浓度为 1%；模拟烟气的二氧化硫的浓度为 6 286 mg/m^3，氧气的浓度为 6%，二氧化碳的浓度为 11%。

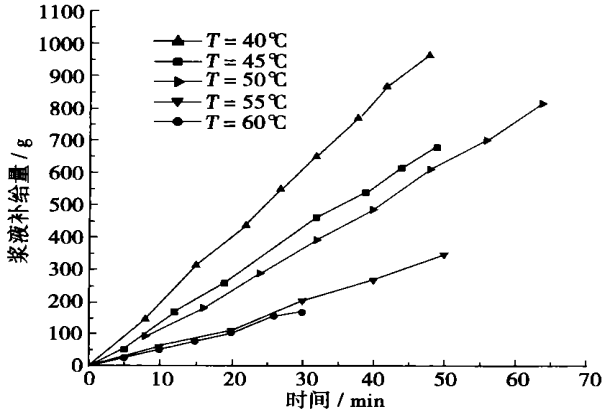

图 2　不同温度下的浆液补给量

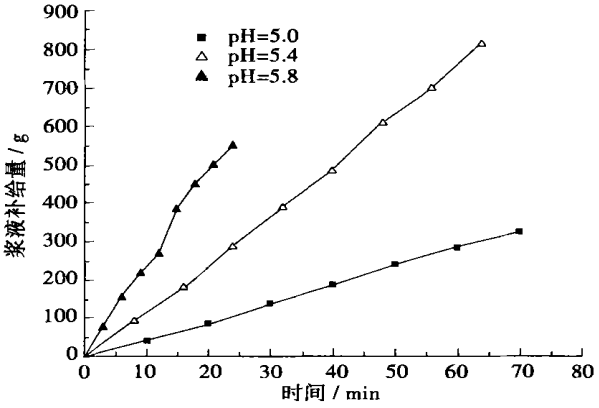

图 3　不同 pH 值下的浆液补给量

图 2 为不同反应温度时的浆液补给量随时间的变化；图 3 为反应瓶在不同反应 pH 值时的浆液补给量随时间的变化；图 4 和图 5 为氟离子和氯离子对石灰石消溶的影响。实验中各工况的进口二氧化硫浓度及模拟烟气总流量相同，出口二氧化硫浓度检测为零。假设进入液相的二氧化硫均只与钙镁离子反应，则可认为各工况与二氧化硫反应的石灰石的量相同。由于图 2～图 5 各工况补给的石灰石浆液速度不同，而各工况与二氧化硫反应的石灰石的量相同，这说明浆液补给速度越快在该条件下石灰石的相对溶解速度越慢，反之，石灰石的溶解速度越快。由图 2 可以看出，在相同的烟气组分和流量下，浆液的补给速度随反应温度的升高而降低，这说明温度越高越有利于石灰石的消溶，这是因为温度越高分子的活化能越强，反应速度越快；同样，由图 3 可以看出，在相同的烟气组分和流量下，浆液的补给速度随反应 pH 值的升高而升高，这说明 pH 值越高越不利于石灰石的消溶，因为 pH 值越高氢离子的浓度越低。由碳酸钙溶解的方程式可以看出，氢离子浓度的降低会抑制碳酸根与氢离子结合形成二氧化碳气体而逸出，从而使溶液中碳酸根离子的浓度升高，增大了碳酸钙溶解反应的阻力。由图 4 可以看出浆液中微量的氟离子不利于石灰石的消溶，这是因为氟离子与溶液中的铝离子形成络合物吸附在

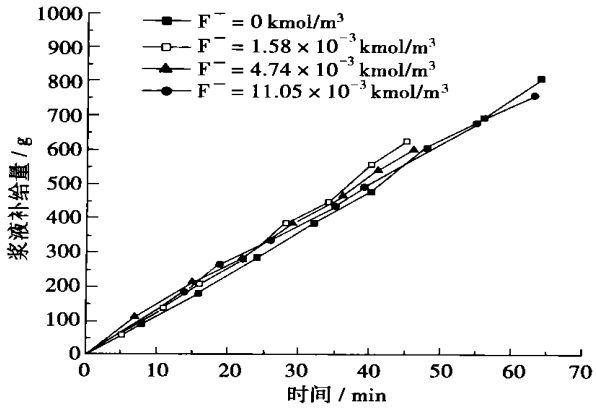

图 4　F^- 对石灰石消溶的影响

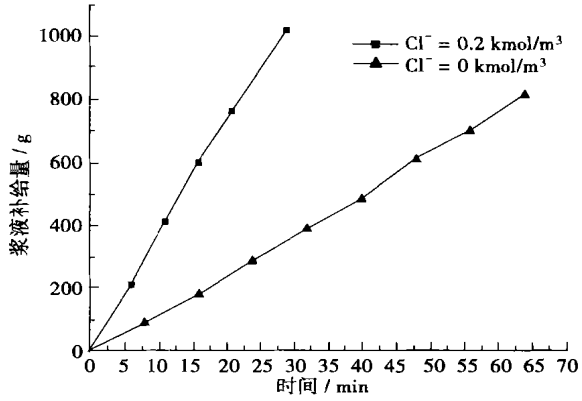

图 5　Cl^- 对石灰石消溶的影响

石灰石的颗粒的表面而阻止石灰石颗粒的继续溶解。由图 5 可以看出浆液中微量的氯离子不利于石灰石的消溶，这与 Ukawa.N 等人的研究结果一致，他们认为氯离子的加入增大了液相的离子强度，使钙离子的扩散系数减小，从而阻止了石灰石的溶解反应[2]。

3.2 公式推导

石灰石的消溶速度与反应的温度、pH 值及未反应的碳酸钙浓度有关。根据质量作用定律和阿仑尼乌斯公式[3]，提出如下的石灰石消溶模型：

$$\mathrm{d}m/\mathrm{d}t = k_{F^-}k_{Cl^-}k\exp\left(-\frac{E}{RT}\right)\left[\frac{C_{H^+}}{C^0}\right]^A\left[\frac{C_{CaCO_3}}{C^0}\right]^B$$

其中：$\mathrm{d}m/\mathrm{d}t$— 单位时间和单位体积内消耗的石灰石的量，l/s；

T— 反应温度，K；

C_{H^+}— 反应瓶中氢离子的浓度，kmol/m^3；

C_{CaCO_3}— 反应瓶中未反应的碳酸钙的浓度，kmol/m^3；

C^0— 标准浓度，$C^0 = 1$ kmol/m^3；

E— 活化能，kJ/kmol；

R— 气体常数，8.314 kJ/(kmol·K)；

A，B— 实验常数；

k_F— 氟离子浓度对反应的影响系数，$k_{F^-} = 1 - 11.742C_{F^-}$，其中 C_{F^-} 为溶液中氟离子浓度，kmol/m^3，此式的适用范围为 $C_{F^-} < 0.001\ 315$ kmol/m^3；

k_{Cl^-}— 氯离子浓度对反应的影响系数，$k_{Cl^-} = 1 - 1.052C_{Cl^-}$，其中 C_{Cl^-} 为溶液中氟离子浓度，kmol/m^3，此式的适用范围为 $C_{Cl^-} < 0.2$ kmol/m^3；

k— 反应的频率因子，可定义为石灰石的活性，L/s，只与石灰石的品种有关，与溶液中的影响离子无关。

将上式两边取对数，得到：

$$\ln\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) = \ln k_{F^-} + \ln k_{Cl^-} + \ln k - \frac{E}{RT} + A\ln\left[\frac{C_{H^+}}{C^0}\right] + B\ln\left[\frac{C_{CaCO_3}}{C^0}\right]$$

根据二氧化硫与碳酸钙的总的反应方程式：

$$SO_2 + CaCO_3 + \frac{1}{2}O_2 + 2H_2O \rightleftharpoons CaSO_4\cdot 2H_2O + CO_2$$

消耗的碳酸钙的摩尔数就等于吸收的 SO_2 的摩尔数；式中 $\mathrm{d}m/\mathrm{d}t$ 等于单位时间内单位体积的浆液吸收的 SO_2 的摩尔数；C_{CaCO_3} 等于单位时间内补给浆液中碳酸钙的摩尔数与消耗的碳酸钙摩尔数的差值再除以反应瓶的体积。

应用此式对实验数据进行线性回归，得到其中的经验常数(见表 2)。

表 2 拟合公式中的各参数值

	k	A	B	E
数值	2.1053×10^{-2}	0.323	0.153	6 739.012

各工况实验数据与拟合公式计算值的对比见图 6。

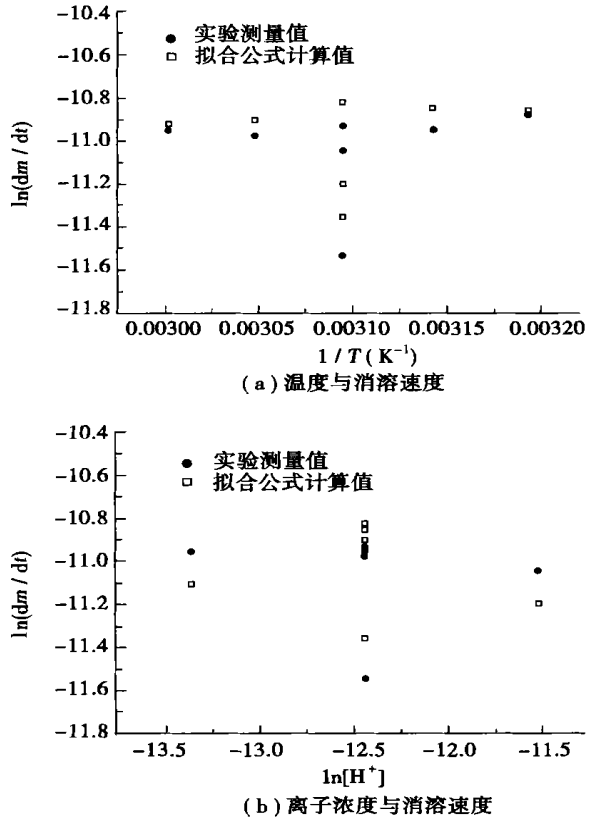

图 6 实验数值与拟合数值的对比

由图 6 可以看出拟合的结果与实验数据较好的吻合，实验误差较小。

4 结 论

(1) 根据质量作用定律和阿仑尼乌斯公式，首次提出了可统一描述石灰石溶解速度的公式 $\mathrm{d}m/\mathrm{d}t = k_{F^-}k_{Cl^-}k\exp\left(-\frac{E}{RT}\right)\left[\frac{C_{H^+}}{C^0}\right]^A\left[\frac{C_{CaCO_3}}{C^0}\right]^B$。该公式物理意义明确，其中 $\mathrm{d}m/\mathrm{d}t$ 表示单位时间和单位体积内消耗的石灰石的无量纲；T 表示反应的温度，K；

C_{H^+} 表示反应瓶中氢离子的浓度, kmol/m^3; C_{CaCO_3} 表示反应瓶中未反应的碳酸钙的浓度, kmol/m^3; C^0 表示标准浓度, C^0 = 1 kmol/m^3; E 表示活化能, kJ/kmol; R 为气体常数, 8.314 kJ/(kmol·K); A, B 为实验常数, k_{F^-} 为氟离子浓度对反应的影响系数; k_{Cl^-} 为氯离子浓度对反应的影响系数; k 表示反应的频率因子, 可定义为石灰石的活性, 反映特定石灰石与二氧化硫反应的能力的大小, 与反应的温度和 pH 无关, k 越大表示该石灰石的活性越强;

(2) 测出了实验中使用的石灰石溶解模型的各参数;

(3) 得出了浆液中微量的氟离子和氯离子均不利于石灰石的溶解;

(4) 利用本文提出的模型可以比较不同石灰石的活性, 从而针对不同品种的石灰石设计合适的浆池大小。

参考文献:

[1] 钟　秦. 燃煤烟气脱硫脱硝技术及工程实例[M]. 北京: 工业出版社, 2002.

[2] UKAWA N, TAKASHINA T, SHINODA N. Effects of particle size distribution on limestone dissolution in wet FGD process application [J]. **American Institute of Chemical Engineers**, 1993, **12**(1): 238—353.

[3] 傅献彩. 物理化学[M]. 北京: 高等教育出版社, 1990.

·信息之窗·

2002 年 ~2011 年燃气轮机市场预测

《Turbomachinery International》2002 ~ 2003 年年度手册报导了 2002 年燃气轮机市场情况, 并对下一个十年(2002 ~ 2011 年)燃气轮机市场状况做了预测。

手册指出, 航空发动机技术正日益增多地应用到工业和船舶燃气轮机, 航空发动机技术正越来越多地结合进重型结构燃气轮机。

大型商船和军用舰船、旅游船和高速渡船、大型货船将是最高输出功率船舶动力的主要用户。14.8 MW 和更大功率等级的船舶燃气轮机大概是 2002 ~ 2011 年间需求的热点, 占总量的 60%。

功率为 11 MW 和更大的燃气轮机的军用市场继续被型号为 LM2500 和 LM2500+ 发动机占有。但是, 由 Rolls—Royce、Northrop Grumman 和 DCF 集团推出的基于 Rolls—Royce RB211 航空涡轮风扇发动机的 WR21 中间冷却回热式推进系统正在向市场中进军。

在大型商船、旅游船、大型旅客渡船和高速货船中日益增多地应用燃气轮机, 燃气轮机的联合装置是航运业呈现的一个发展趋势。

(吉桂明　供稿)

近期多相流过程层析成像技术的发展＝**Recent Developments in Process Tomography for Multi-phase Flows** [刊, 汉] / ZHANG Xiu-gang, WANG Dong, LIN Zong-hu (College of Energy &Power Engineering under the Xi'an Jiaotong University, Xi'an, China, Post Code: 710049) //Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). — 221～226

Process tomography for multi-phase flows plays a major role in the exhaustive exposition of multi-phase flow basic laws, promoting the development of multi-phase flow theories and their engineering applications. The authors give a brief account of the use and development of several types of tomographic techniques as represented by X and γ rays, ultrasonic waves, electric resistance, capacitance and mesh electrodes in the detection and measurement of multi-phase flow parameters. An analysis is given of a variety of key issues, such as image reconstruction, the design and selection of sensors, real-time character, etc. In conclusion, application prospects and development trends of the process tomography are forecast. **Key words**: process tomography, two-phase flow, multi-phase flow, image reconstruction, on-line measurement

电除尘器阴极收尘潜力的研究＝**A Study of the Dust Removal Potential by the Cathode of an Electrostatic Precipitator** [刊, 汉] / HU Man-yin, GAO Wei-ying, BAI Zheng-guang, et al (Department of Environmental Engineering, North China Electric Power University, Baoding, China, Post Code: 071003) //Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). — 227～229

A preliminary analysis and an experimental study were performed of the various functions of the cathode of an electrostatic precipitator. They include: corona discharge, the establishment of a high field intensity, dust collection, the reduction of secondary dust-emission loss, the weakening and elimination of counter-corona harmful effects as well as the prevention of low voltage and high current-related unfavorable operations. It is suggested that cathode structure improvement can lead to a reduction of the cathode secondary dust-emission loss and the enhancement of the cathode dust-collection effectiveness as well as to a suppression of counter-corona. Meanwhile, it is also conducive to a stable operation of the electrostatic precipitator under the condition of a high voltage and relatively low current, thus achieving the aim of high dust-removal efficiency. The resolution of the above-mentioned issues can provide helpful reference data for the design, modification and operation of electrostatic precipitators. **Key words**: electrostatic precipitator, dust removal by a cathode, cathode secondary dust-emission

一种新的湿法脱硫强制氧化技术＝**New Technology of Forced Oxidation for a Wet Flue-gas Desulfurization System** [刊, 汉] / TIAN Feng-guo, ZHANG Ming-chuan (College of Mechanical &Power Engineering under the Shanghai Jiaotong University, Shanghai, China, Post Code: 200240), MA Chun-yuan (College of Energy &Power Engineering under the Shandong University, Jinan, China, Post Code: 250061), WU Jiang (Materials Characterization Center under the Western Kentucky University, KY 42101, USA) //Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). — 230～233

Forced oxidation plays a key role in the prevention of agglomeration and blockage in a wet flue-gas desulfurization (WFGD) system and the reduction of secondary pollution caused by desulfurization waste dregs. A jet-flow aeration technique is proposed for use in the forced oxidation process of limestone/gypsum WFGD system. Moreover, a theoretical analysis is conducted of the gas/liquid interphase mass-transfer features of the jet-flow aeration forced-oxidation process by the use of a dual film theory. The results of the analysis indicate that a jet-flow aerator as a kind of mixing device for the chemical reaction mass-transfer of gas/liquid two-phase media can give full play to its intensive mixing action, thus enhancing energy comprehensive utilization rate. The calculation results of the energy consumption of a WFGD project show that the adoption of the jet-flow aeration mode has resulted in energy-savings of more than 20%. The reduction of desulfurization cost is conducive to promoting the domestic manufacture of key desulfurization equipment. **Key words**: wet flue-gas desulfurization, forced-oxidation process, jet-flow aeration

微型鼓泡床中石灰石溶解特性的实验研究＝**Experimental Investigation of Limestone Dissolution Characteristics in a Micro-sized Bubbling Bed** [刊, 汉] / SHI Zheng-hai, ZHAO Cai-hong, ZHOU Qu-lan, et al (College of En-

ergy &Power Engineering under the Xi'an Jiaotong University, Xi'an, China, Post Code: 710049) // Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). —234~237

By using gas in a steel cylinder to simulate flue gas during tests investigated was the impact on the dissolution rate of limestone exerted by the following factors: gas pH value and temperature of reaction in a micro-sized bubble bed and minute quantity of fluorine and chlorine ions in slurry. On the basis of mass action law and arrhenius equation a mathematical formula is proposed for calculating the limestone dissolution rate. With the physical meaning of various parameters being clarified it is possible to make a unified description of the limestone dissolution rate under various operating conditions. Meanwhile, various parameters of the dissolution rate of the limestone used during the tests were determined with a conclusion that the micro quantities of fluorine and chlorine ions are unfavorable to the dissolution of limestone. By making use of the model proposed by the authors it is feasible to compare the reactivity of different types of limestone and to design slurry tanks of appropriate size to suit various kinds of limestone. This is of great significance for the study of a wet flue-gas desulfurization process. **Key words**: limestone, dissolution rate, bubbling bed

闪蒸处理对石灰石脱硫性能的影响= **The Impact of Flash Evaporation Modification on the Desufurization Performance of Limestone Particles** [刊, 汉] / CHEN Chuan-min, ZHAO Chang-sui, HAN Song, et al (Education Ministry Key Laboratory of Clean Coal Power Generation and Combustion Technology under the Southeastern University, Nanjing, China, Post Code: 210096) // Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). — 238~241

On a solid-particle pore diameter enlargement device constructed by the authors flash-evaporation modification tests on limestone particles were performed and an experimental investigation of calcination and desulfurization was carried out on samples in a gas-flow reactor. It is found that the flash-evaporation modification treatment may lead to an increase in limestone pore diameter. In addition, with the enlargement of limestone pore diameter the cross-linkage properties among the pores will be enhanced, resulting in a slight decrease in specific surface area. The pore diameter of calcination product CaO after the flash-evaporation modification of the limestone will shift in the direction of securing a larger pore size. In the meantime, due to the flash-evaporation modification the transport performance of the reaction gas has been significantly improved, thus decreasing the sintering effect in the calcination process. As a consequence, the specific surface area will be increased considerably. Under identical test conditions the desulfurization efficiency of samples after the flash-evaporation modification has been markedly enhanced. **Key words**: flash evaporation, modification, limestone, pore structure, desulfurization

不同煤种混煤燃烧时 NO_x 生成和燃尽特性的试验= **Experimental Research of the NO_x Generation and Burnout Characteristics During the Combustion of Blended Coals** [刊, 汉] / WENG An-xin, ZHOU Hao, CEN Ke-fa (Research Institute of Thermal Energy Engineering under the Zhejiang University, Hangzhou, China, Post Code: 310027), ZHANG Li (Hunan Electric Power Prospecting and Design Institute, Changsha, China, Post Code: 410007) // Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). —242~245

The combustion characteristics of various coals (anthracite, lean coal and bituminous coal) and their blends were investigated in a one-dimensional sedimentation furnace. The impact on NO_x emissions of various factors was analyzed along with a discussion of the effect on burnout rate of different excess air factors, mixing/dilution ratios and the ratio of primary and secondary air. Test results indicate that when bituminous coal accounts for 25% of the blended coals the NO_x emissions are relatively low. In case of burning blended coals there emerged several NO_x emission peaks along the axis of the furnace, which are caused by the different characteristics of the coals taking part in the combustion. **Key words**: blended coal, NO_x emission, mixing/dilution ratio, burnout rate

煤的模型化合物热解过程中HCN、NH_3 的逸出规律= **The Law of HCN and NH_3 Escape during the Pyrolysis of Model Compounds of Coal** [刊, 汉] / ZHAO Ke, TAN Hou-zhang, ZHOU Qu-lan, et al (Xi'an Jiaotong University, Xi'an, China, Post Code: 710049) // Journal of Engineering for Thermal Energy &Power. — 2004, 19(3). —246~248