

烟道喷浆脱除烟气中二氧化硫的试验研究*

陆永琪 郝吉明

侯栋歧 于荣华

(清华大学环境工程系, 北京 100084)

(哈尔滨电站设备成套所, 哈尔滨 150046)

摘要 在长 3.5 m、断面积为 150 mm×150 mm 的立式反应器中进行了烟道喷石灰浆和电石渣浆脱除烟气中 SO₂ 的模拟试验, 得出了出口温距、钙硫摩尔比、雾化气液比、SO₂ 入口浓度、烟气入口温度和气体停留时间对脱硫效率的影响规律。试验还表明, 当 $\Delta T = 18^\circ\text{C}$, Ca/S=1.5 时, 系统脱硫效率可达 65%。同时, 建立了反应预测模型 $\eta = 1 - [(T_1 - T_{\infty}) / (T_0 - T_{\infty})]^{-\frac{\alpha}{1+\beta}}$, 其中参数 α 和 β 采用共轭梯度法估值, 模型预测值与实测值的平均相对偏差低于 7%。

关键词 烟道喷浆, 烟气脱硫, 雾化。

烟道喷浆烟气脱硫技术与常规的喷雾干燥法在不少方面极为相似, 不同之处在于前者以烟道直接作为反应器进行 SO₂ 脱除, 不需要另外的吸收容器, 使工艺投资大大降低、操作简化及场地需要减少^[1], 因此十分适合在中国开发应用。尽管该技术已被美国能源部列入洁净煤技术示范项目^[2], 但在国内的研究开发还少见报道。本文通过模拟试验研究, 系统考察和分析了各工艺变量对脱硫效率的影响规律, 旨在为工艺放大和工业化应用提供依据。

1 实验装置及方法

1.1 实验装置

实验装置见图 1。空气经液化石油气燃烧加热, 并与一定量的纯 SO₂ 钢瓶气相混, 配得所需浓度的模拟烟气。雾化浆滴喷入反应器后, 被烟气所夹带, 边蒸发边反应。反应器全长为 3.5 m, 方形断面积为 150 mm×150 mm。净化烟气经旋风分离器除尘, 由引风机放空。

1.2 浆液制备及计量

实验使用的石灰和电石渣有效钙含量(以 CaO 计)分别为 92.6% 和 57.6%, 经筛分粒度均小于 100 μm 。熟化时, 温度控制在 90℃ 附近, 与蒸馏水的重量比控制为 1:4。熟化后,

以自来水将其稀释成所需浓度。浆液流量由调节料液槽高度控制, 设置节流管可增加浆量调节的灵敏度。

1.3 雾化喷嘴

本试验研制了一种新型的双流体喷嘴, 其工作原理是: 雾化气从内管射孔高速喷出, 将溢过射孔的浆液高度分散。测试表明, 喷嘴雾化半角为 10°, 典型工况下的 Sauter 平均粒径约为 75 μm 。

1.4 测量仪表

烟气流量由靠背管测量; 干、湿球温度分别由普通水银温度计和湿球温度计测得; 雾化气和 SO₂ 气量由转子流量计调节; SO₂ 浓度采用北京市劳保所 BRY-1 型 SO₂ 分析仪和北分厂 MSI-2000 型烟道气分析仪进行比较测量。

1.5 实验参数

试验运行参数为: 烟气流量 61.8、42.6 Nm³/h; 入口烟气温度 150℃、130℃; 气体停留时间为 3.3、4.4 s; SO₂ 入口浓度 4000、2857 mg/m³; 钙硫摩尔比 0.3—2.8; 温距 18—54℃; 雾化气液比 0.06—0.18 m³/kg。

* 国家“八五”科技攻关项目

收稿日期: 1996-05-22

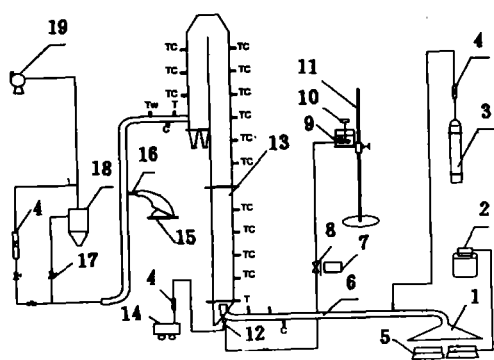


图1 烟道喷浆脱硫实验装置

1. 集气罩 2. 煤气罐 3. SO₂钢瓶 4. 转子流量计 5. 灶具 6. 引风管 7. 振动器 8. 节流管 9. 浆液槽 10. 搅拌器 11. 高度调节杆 12. 喷嘴 13. 反应器 14. 空压机 15. 斜压计 16. 靠背管 17. 阀门 18. 旋风除尘器 19. 引风机

T. 温度测点 C. 浓度测点

2 反应模型

假定气体在反应器中呈柱状流流动,且浆滴均匀地分散于气体中。SO₂浓度改变及浆滴中水分蒸发对烟气密度影响很小,可忽略不计。这样,反应器微元高度内的物料衡算式可写为:

$$-v\rho_g dy = K_g a P_i y dl \quad (1)$$

$$\text{即, } \frac{dy}{y} = -\frac{K_g a P_i}{\rho_g} \frac{dl}{V} = -\frac{K_g a P_i}{\rho_g} dt \quad (2)$$

式中: V : 气体速度; ρ_g : 气体摩尔密度; y : SO₂摩尔分数; K_g : 气相总传质系数; a : 单位体积气流中的液滴表面积; P_i : 气体总压; l : 反应器长度; t : 有效反应时间。

为简化过程模拟,作如下假定:(1)因受蒸发作用的影响,单位体积气流中的液滴表面积沿反应器高度是变化的,但由于浆液中悬浮小颗粒的存在,其值在整个蒸发和反应过程中的变化并不很大^[3],假定可按常量处理且正比于初值 a_0 ;(2)有效反应时间并不是指烟气在反应器的实际停留时间,而是指发生脱硫反应的有效时间,由于干颗粒与SO₂的反应速率极为缓慢^[4],有效时间假定为浆滴的蒸干时间;(3)气相总传质系数包含了气相传质分系数 K_g 和液相^{传质分系数 K_l} 的共同影响,由于蒸发过程

中浆滴直径变化不大,假定 K_g 近似不变;浆液中悬浮颗粒浓度的增加将减少液膜厚度和提高悬浮粒的溶解速率^[5],因此 K_l 随钙硫摩尔比的增加而增加,假定两者呈正比关系。根据以上假设,由式(2)最终可求得:

$$\eta = 1 - \frac{y_i}{y_0} = 1 - \left(\frac{T_i - T_{as}}{T_0 T_{as}} \right)^{-\frac{\alpha R}{\beta + R}} \quad (3)$$

式中, $\alpha = c K_g P_i / \rho_g$; $\beta = \frac{H K'_g}{K'_l \phi}$; c : 系数; K'_l : Ca/S=1时的液相传质分系数; H : 亨利系数; ϕ : 增强因子; R : 钙硫摩尔比; T_i : 烟气入口温度; T_0 : 烟气出口温度; T_{as} : 烟气绝热饱和温度; y_i : SO₂入口摩尔分数; y_0 : SO₂出口摩尔分数; η : 脱硫效率。系数 α 和 β 为可调参数,采用共轭梯度法进行非线性最优化估值。

3 结果讨论与分析

3.1 出口干湿温距的影响

出口干湿球温距反映了出口温度与绝热饱和温度的接近程度,如图2所示,它是影响脱硫效率的一个重要因素。反应器出口温度越低,温距越小,说明喷入反应器的浆液含水量越大。含水量提高,一方面由于迅速蒸发而减少了传热推动力,另一方面也提高了烟气的相对湿度,这都将使浆滴完全蒸发所需时间大大延长^[6],从而增加了气液之间的有效反应时间,使脱硫效率提高。

3.2 Ca/S摩尔比的影响

由图2可见,脱硫效率随Ca/S摩尔比的增加而增加,但变化幅度逐渐减缓。Ca/S摩尔比的增加实际意味着浆液中悬浮颗粒浓度的增加,这有利于减小液膜的扩散阻力和悬浮颗粒的溶解阻力,从而使反应速率提高。但随着脱硫反应的进行,反应产物逐渐沉积在悬浮颗粒表面,最终将出现反应盲区,影响进一步反应。因此,脱硫效率随Ca/S摩尔比的提高幅度是逐渐减少的。

3.3 浆滴雾化质量的影响

对于双流体喷嘴,影响浆滴雾化质量(平均直径和粒径分布)的主要变量是气液比。实测气

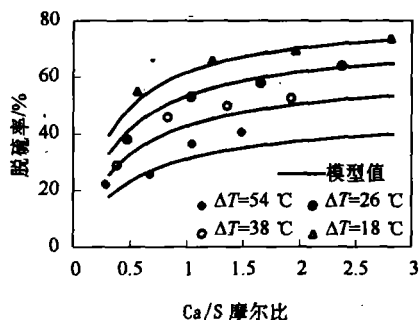


图2 ΔT 和 Ca/S 摩尔比对脱硫率的影响
入口烟温 150℃, 初始 SO_2 浓度 4000 mg/m^3 ,
风量 61.8 Nm^3/h , 石灰浆液

液比范围内对应的 Sauter 平均粒径位于 60—110 μm 之间. 粒径的变化可带来 2 种不同的影响. 首先, 增大粒径可延长蒸发时间, 对反应是有利的; 另一方面, 粒径增大将使浆滴总反应表面积减少, 对反应又是不利的. 由图 3 可见, 正效应要稍大于负效应, 即随着气液比的减少 (粒径增加), 脱硫效率略呈增加趋势.

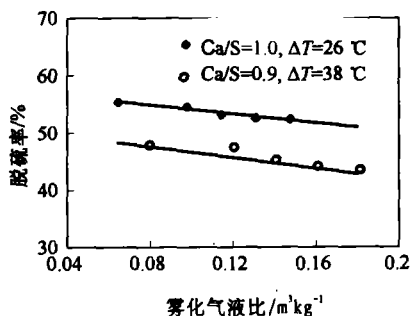


图3 喷嘴气液比对脱硫效率的影响
入口烟温 150℃, 初始 SO_2 浓度 4000 mg/m^3 ,
风量 61.8 Nm^3/h , 石灰浆液

3.4 SO_2 进口浓度的影响

图 4 给出了进口 SO_2 浓度对脱硫效率的影响. SO_2 初浓度 4000、2857 mg/m^3 相当于燃煤含硫 1.3%—1.8% 的烟气. 由图 4 可见, 脱硫效率随着 SO_2 进口浓度的增加而略有下降. 根据气液溶解平衡理论易知, 增大 SO_2 气相分压将使液相的溶解分率减少, 因而降低了反应速率.

3.5 烟气入口温度的影响

离开空气预热器的锅炉烟气温度一般在 120—180℃ 的范围内, 本研究的试验温度为

130℃ 和 150℃. 提高烟气入口温度可增加脱硫效率, 如图 5 所示. 较高的烟气入口温度允许喷入更多的浆液, 因此也就增大了浆滴的反应总表面积, 有利于脱硫反应速率的增加.

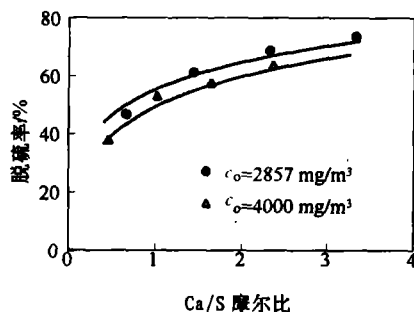


图4 SO_2 进口浓度对脱硫效率的影响
入口烟温 150℃, $\Delta T=26^\circ\text{C}$,
风量 61.8 Nm^3/h , 石灰浆液

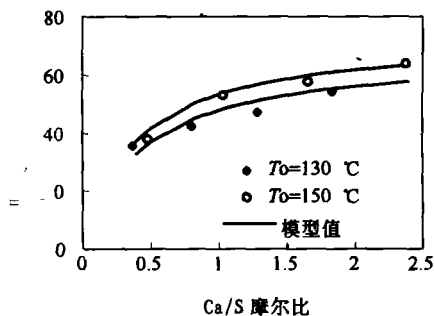


图5 烟气入口温度对脱硫效率的影响
 $\Delta T=26^\circ\text{C}$, 初始 SO_2 浓度 4000 mg/m^3 ,
风量 61.8 Nm^3/h , 石灰浆液

3.6 烟气停留时间的影响

实验中通过调节烟气流量来改变烟气停留

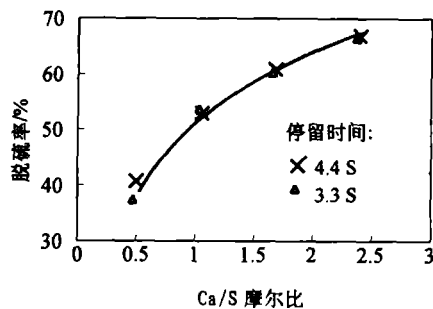


图6 烟气停留时间对脱硫效率的影响
入口烟温 150℃, $\Delta T=26^\circ\text{C}$, 初始 SO_2 浓度
4000 mg/m^3 , 石灰浆液

时间. 由图 6 可见, 停留时间由 3.3 s 增至 4.4 s, 脱硫率变化没有显示出规律性. 这也表明: 由于 SO_2 的脱除大部分都发生在 1—2 s 的浆滴蒸发期内^[7], 停留时间的增加不足以产生明显的脱硫效率提高.

3.7 吸收剂的影响

图 2 至图 6 均是石灰浆液的试验结果. 图 7 给出了电石渣浆的脱硫试验结果. 比较图 2 和图 7 不难发现, 电石渣显示了与石灰相当的脱硫活性. 电石渣中的主要成分是 $\text{Ca}(\text{OH})_2$, 制浆时不象石灰那样发生颗粒爆裂, 但其颗粒有较大的比表面积, 富含空隙, 易于溶解和反应.

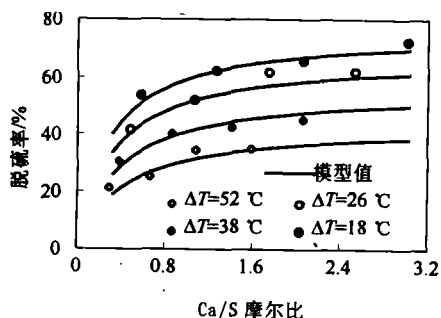


图 7 电石渣浆脱硫特性

入口烟温 150℃, 初始 SO_2 浓度 4000 mg/m³,
风量 61.8 Nm³/h, 电石渣浆

3.8 模型计算结果比较

模型待定参数 α 代表的是系统性质, β 代表的是液滴反应过程中液膜阻力与气膜阻力之比. 最优化估值结果表明, 对石灰浆液, $\alpha=0.916$, $\beta=0.707$; 对电石渣浆液, $\alpha=0.789$, $\beta=0.569$. 由 β 值可知, 反应过程中液膜阻力约占总传质阻力的 40% 左右.

模拟计算值与实测值的比较见图 8(a) 和 (b), 两者显示了较好的吻合性, 平均相对偏差分别为 6.27% 和 4.12%.

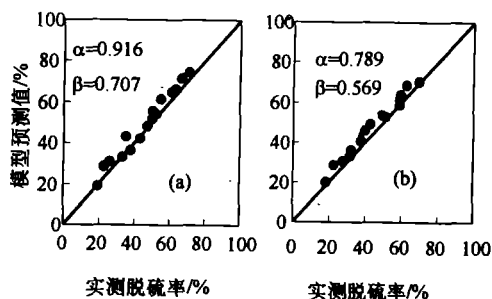


图 8 模拟计算值与实测值的比较

(a) 石灰浆 (b) 电石渣浆

4 结论

(1) 当 $\Delta T=18^\circ\text{C}$, $\text{Ca}/\text{S}=1.5$ 时, 系统脱硫率可达 65%.

(2) 出口干湿球温距和 Ca/S 摩尔比对脱硫效率影响显著, 烟气入口温度、 SO_2 入口浓度和喷嘴气液比对脱硫效率有中等程度的影响, 而烟气停留时间的影响不显著.

(3) 电石渣浆与石灰浆具有相当的反应活性, 电石渣可用作烟道喷浆法脱硫的吸收剂.

(4) 模型计算值与实测值的平均相对偏差低于 7%, 反应模型可用于烟道喷浆法脱硫的模拟.

参 考 文 献

- 1 Keeth R J et al. . Economic Evaluation of Flue Gas Desulfurization Systems (EPRI Project Report). Volume 1, Section 19. 1991: 1—26
- 2 U. S. Department of Energy. Clean Coal Technology Demonstration Program (Program Update 1994). 1995: 5—23
- 3 Harriot P J. Air Waste Manage. Association, 1990, 40(7): 998
- 4 Jorgensen C. Environmental Progress, 1987, 6(2): 26
- 5 George P et al. . Chem. Eng. Comm., 1990, 96: 97
- 6 张新生等编. 燃烧烟气脱硫. 北京: 中国地质大学出版社. 1991: 205—211
- 7 Newton G H et al. . AIChE Journal, 1990, 36(12): 1865

System Eng. & Research Institute, Harbin 150046): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 16–19

The experiment was conducted in a vertical reactor with a total length of 3.5 m and cross section of 150 mm × 150 mm to simulate flue gas desulfurization with lime and carbide lime slurry injection in the duct. Effects on SO₂ removal were found, of such as the approach to adiabatic temperature at the exit, molar ratio of Ca to S, flux ratio of atomizing gas and slurry, gas inlet temperature, SO₂ initial concentration and gas residence time. Also, it was showed experimentally that SO₂ removal can achieve 65% at $\Delta T = 18^\circ\text{C}$ and Ca/S = 1.5. In addition, a reaction model was developed, i. e., $\eta = 1 - [(T_i - T_w)/(T_0 - T_w)]^{1/\beta} - \frac{\alpha}{\beta} k$, where α and β as equation parameters were determined by the conjugate gradient optimization method, and model predictions agree well with the experimental values with relative errors lower than 7%.

Key words: duct slurry injection, flue gas desulfurization, atomization.

Design of an Annular Denuder to Measure Atmospheric Ammonia. Tian Honghai et al. (Peking University, Beijing 100871): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 20–23

A new trace gases sampler, annular denuder (AD), was developed and evaluated for the first time in China. Theoretical consideration was given and quality tests have been executed for designed AD. Its absorption efficiency for ammonia is over 97% and the detection limit is down to 0.15 $\mu\text{g}/\text{m}^3$ (10 m³ sample volume). The intercomparisons of AD with filter pack as well as wet AD methods showed good agreement with one another. In springs of 1985 to 1992, the atmospheric NH₃ concentrations have been measured in Zhong Guancun District in Beijing City. The results range from 4.6 to 40 $\mu\text{g}/\text{m}^3$ with the average of 17 $\mu\text{g}/\text{m}^3$.

Key words: annular denuder, ammonia, determination of atmospheric ammonia.

The Evaluation of Economic Loss by the Acid Deposition Pollution in Chongqing. Chen Nian and Yun Qihou (Dept. of Geography, Southwest China Normal University, Chongqing 630715): *Chin. J. Environ. Sci.*, **17**(5), pp. 24–27

Acid deposition pollution in Chongqing is very serious. In order to define its economic losses, to provide a foundation for the decision making of economic and social development and to select a satisfied control plan, based on investigations in human health and damage of agriculture forest pollution, on tests of materials exposed and simulated experiment of acid deposition, using the methods of market-prices, wages costs and input-output comparison between benefits and losses, the author assessed its economic losses. The total economic losses caused by acid deposition in 1990 and 1994 are 504 million yuan and 1188 million yuan respectively, which are 2.47% and 2.0% of the GNP of the same years. The striking difference in the losses between the two years is caused mainly by the price factor.

Key words: acid deposition, economic loss, evaluation.

Fe-Si Sulfur Capture Promotion During Coal Briquet Combustion. Lin Guozhen et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 28–29

In this paper, A new Fe-Si promoter for sulfur capture was proposed for coal-briquet combustion at high temperature. Characterization of the slag left after combustion has been carried out by means of X-ray powder diffraction. A new phase $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$ was identified, which is thermally stable. This might explain its stabilizing role in sulfur fixation.

Key words: coal briquet, sulfur capture, XRPD.

COD and BOD₅ Removal Efficiencies in a Pilot Scale Constructed Reed Bed Receiving Cheese-Processing Wastewater. Huichang Zhu (Huan Qiu Environmental Engineering Co. Shanghai 201203), D. K. Stevens (Utah State University, UT84322, USA): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 30–32

Under the influent COD concentration between 400–800 mg/L and temperature between 15–23°C, the constructed wetland functioned efficiently for COD removal. COD mass removal efficiencies reached 97 to 98%, and total removal rates reached 23.3 to 28.2 g/m² · d. BOD₅ mass removal efficiencies reached 97 to 99%, while total removal rates reached 12.6 to 17.2 g/m² · d. The influent trench played an important role in COD and BOD₅ removal. Nearly 70 to 90% of the COD and BOD₅ removal occurred in the influent trench. During the entire experimental period, the reed bed effluent water quality met secondary discharge standards if there was no pH shock loading.

Key words: constructed wetland, subsurface flow, reed bed, control bed.

The Study on Regeneration Efficiency of Ion Exchange Resins to Enhance Nitrate Elimination. Gong Wenli et al. (Institute of Environmental Engineering Technology, Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 33–35

The enhanced nitrate elimination from groundwater by modifications of the CARIX process was described. For raw water with relative low hardness and elevated nitrate concentrations, the process was simplified by applying only an anion exchanger. In the service cycle, sulfate and nitrate species were replaced by bicarbonate species. In the regeneration step, the resin was converted into bicarbonate form by carbonic acid and magnesium oxide. Results of experiments in the laboratory scale have demonstrated that regeneration efficiency is improved apparently by adding magnesium oxide during regeneration. The optimum concentration of magnesium oxide was 0.4%. In this case, all of the resins used in the tests gained the average reduction of nitrate above 50%.

Key words: CARIX process, nitrate carbon dioxide, drinking water.