

简易干法烟气脱硫技术的试验研究*

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摘要 为了开发研究低投资、低成本的脱硫方法, 在研制高活性多孔脱硫剂的过程中, 研究了各种因素的影响, 并对脱硫剂进行物化特性的表征。脱硫剂比表面积可达 $41 \text{ m}^2/\text{g}$, 粒径分布: $0-10 \mu\text{m}$ 占 24.1%; $10-20 \mu\text{m}$ 占 20.1%; $20-40 \mu\text{m}$ 占 29.0%; $40 \mu\text{m}-60 \mu\text{m}$ 占 16.6%; $60-90 \mu\text{m}$ 占 10.3%。实验室小试, 用固定床反应器模拟研究干法烟气脱硫反应过程, 烟气相对湿度、脱硫剂比表面积、反应温度等为影响脱硫剂与 SO_2 反应的主要因素。初步中试结果表明: 烟气处理量 $1000 \text{ m}^3 \cdot \text{h}^{-1}$, SO_2 浓度 $1430 \text{ mg} \cdot \text{m}^{-3}-4290 \text{ mg} \cdot \text{m}^{-3}$, Ca/S 摩尔比 1.5—1.8 条件下, SO_2 去除率为 60%—70%。此项技术, 流程简单, 投资少, 成本低, 获得中等水平的脱硫效果。

关键词 简易干法烟气脱硫, 脱硫剂, 小试, 中试。

最早的烟气脱硫技术为湿法^[1, 2], 其特点是技术成熟, 操作经验丰富, SO_2 去除率高达 95% 以上。但不足之处设备庞大, 投资费用昂贵、大量废物的再处理亦是问题, 难于接受。干法烟气脱硫为一种简便方法^[3-7]。

为了进一步提高干法脱硫率, 笔者研制成功高效多孔细粉脱硫剂, 并进行了与 SO_2 反应研究。定量地确定影响 SO_2 去除率和脱硫剂利用率主要因素; 优化系统的性能降低成本为工业化应用提供理论依据和设计参数。

1 实验部分

1.1 高效多孔细粉脱硫剂研制^[8]

(1) 实验方法 将一定量的添加剂放入盛有 100 ml 蒸馏水的锥形瓶中, 将锥形瓶置于水浴中, 以维持一定的温度, 再加入一定量的 CaO (分析纯, CaO 含量不少于 98.0%), 应用磁力加热搅拌器, 控制加热温度与搅拌速度和反应时间, 使其水解反应进行完全, 进行过滤, 然后在 130°C 烘箱中烘干即为产品。

(2) 高效多孔细粉脱硫剂的表征 脱硫剂比表面积用 BET 方法测定; 脱硫剂粒径分布用英国 Malvern 2600 型激光粒径分析仪测定。

1.2 实验结果

(1) 实验室小试 实验装置见图 1。

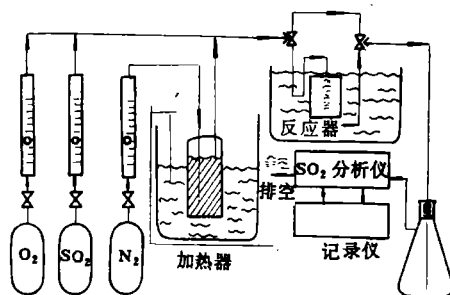


图1 实验室小试装置

(2) 中间试验装置 试验装置见图 2。

2 实验结果与讨论

2.1 高效多孔细粉脱硫剂制备与表征

(1) 添加剂的含量对比表面积的影响 CaO 5 g, 反应温度 40°C , 反应时间 1 h, 实验结果如图 3。结果表明, 随着添加剂的量增加, 吸硫剂比表面积也增加。当添加剂的量超过 3% 时, 其比表面积的数值迅速下降, 故可以认为比较适宜的添加剂的重量百分比为 3%。

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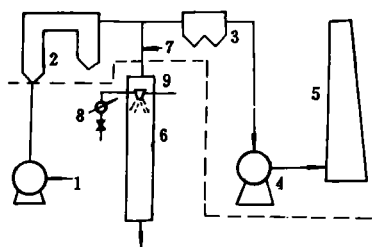


图2 简易干法烟气脱硫中试装置

1. 鼓风机 2. 锅炉($4 \text{ t} \cdot \text{h}^{-1}$) 3. 多管旋风除尘器
4. 引风机 5. 烟囱 6. 喷钙脱硫反应器
7. 喷钙加料口 8. 自来水表 9. 水喷嘴

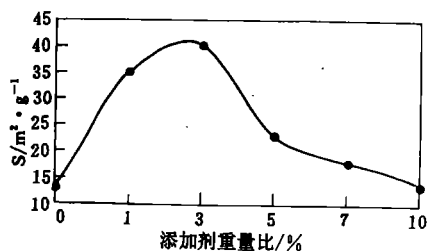


图3 添加剂的含量对比表面积的影响

(2) 反应温度对比表面积的影响 CaO 4.5 g ，反应时间 1 h ，添加剂 3% (重量)，实验结果如图4。结果表明，随着温度的增加，脱硫剂比表面积迅速增加，温度上升到 40°C 以后比表面积又随着温度的增加而降低，至 50°C 出现最低谷，到 60°C 又出现一个比表面积较高的峰，所以比较适宜的温度在 40°C 左右和 60°C 左右。

(3) 高效多孔细粉脱硫剂的表征 脱硫剂粒径测定结果可看到，粒径分布比较均匀，粒径 $0-20 \mu\text{m}$ 占 44.1% ； $20-40 \mu\text{m}$ 占 29.0% ； $40-60 \mu\text{m}$ 占 16.6% ； $60-90 \mu\text{m}$ 占 13.3% ，以细粒为主。

不同条件下研制的脱硫剂比表面积测定结果为 $41.00-13.01 \text{ m}^2/\text{g}$ 。

2.2 高效多孔细粉脱硫剂与 SO_2 吸附反应

(1) 相对湿度(RH)对 $\text{Ca}(\text{OH})_2$ 转化率的影响 图5为不同相对湿度条件下， $\text{Ca}(\text{OH})_2$ 转化率随时间变化曲线。可以明显看出 $\text{Ca}(\text{OH})_2$ 转化率随相对湿度增加而增加。

(2) SO_2 浓度对 $\text{Ca}(\text{OH})_2$ 转化率的影响 影响结果见图6，可以看到 $\text{Ca}(\text{OH})_2$ 转化率与 SO_2 入口浓度成正比。

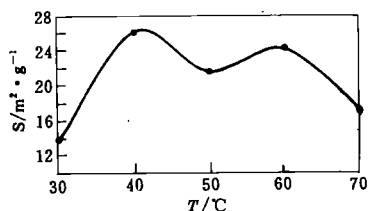
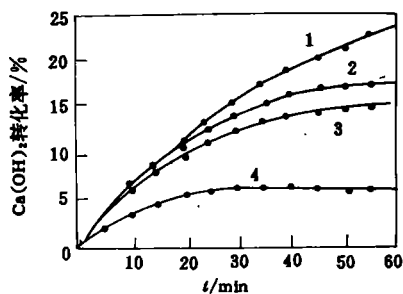


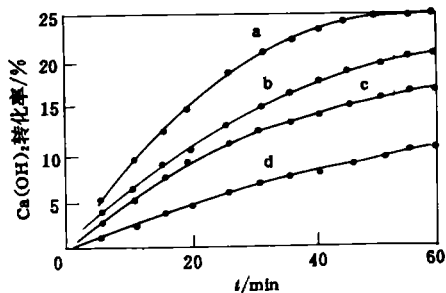
图4 反应温度对比表面积的影响

图5 相对湿度对 $\text{Ca}(\text{OH})_2$ 转化率的影响

实验条件： 2 L/min ， SO_2 1.0 L/min ，

SO_2 浓度 $5720 \text{ mg} \cdot \text{m}^{-3}$ ， $\lg \text{Ca}(\text{OH})_2$ ，温度 60°C 。

1. RH 70.9% 2. RH 59.0% 3. RH 46.9% 4. RH 28.5%

图6 SO_2 浓度对 $\text{Ca}(\text{OH})_2$ 转化率的影响

实验条件：空气 1.2 L/min ， SO_2 1.0 L/min ，

RH 58%，反应温度 60°C ， $\lg \text{Ca}(\text{OH})_2$

SO_2 浓度：a. $5720 \text{ mg} \cdot \text{m}^{-3}$ b. $4150 \text{ mg} \cdot \text{m}^{-3}$

c. $2860 \text{ mg} \cdot \text{m}^{-3}$ d. $1570 \text{ mg} \cdot \text{m}^{-3}$

(3) 反应温度对 $\text{Ca}(\text{OH})_2$ 转化率的影响 实验结果如图7所示。

结果表明： $\text{Ca}(\text{OH})_2$ 的转化率随反应温度升高而增加，并呈指数增加。

(4) 脱硫剂比表面积对 $\text{Ca}(\text{OH})_2$ 转化率的影响 结果如图8所示，可以看出，比表面积越大， $\text{Ca}(\text{OH})_2$ 转化率越高，反应速度越快。

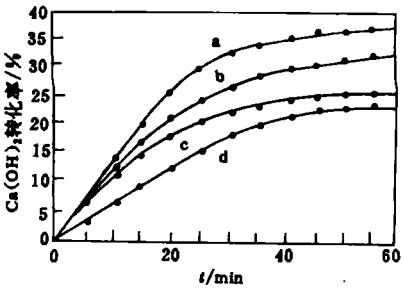


图 7 反应温度对 $\text{Ca}(\text{OH})_2$ 转化率的影响
实验条件为: 空气 1.2 L/min, SO_2 1.0 L/min,
RH58%, SO_2 入口浓度 $5720 \text{ mg} \cdot \text{m}^{-3}$, lg $\text{Ca}(\text{OH})_2$
a. 70°C b. 60°C c. 50°C d. 40°C

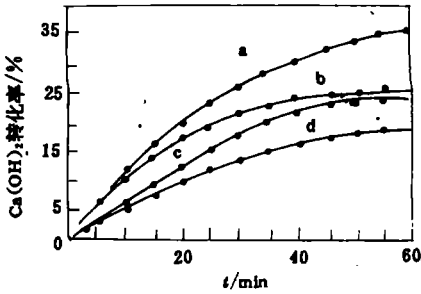


图 8 不同比表面积(S)对 $\text{Ca}(\text{OH})_2$ 转化率的影响实验条件
为: 空气 1.2 L/min, SO_2 1.0 L/min, RH 58%, SO_2 入口
浓度 $5720 \text{ mg} \cdot \text{m}^{-3}$, 温度 60°C, lg $\text{Ca}(\text{OH})_2$
a. $S=34.85$ b. $S=22.95$ c. $S=18.54$ d. $S=13.01$

2.3 中间试验

中间试验装置安装在笔者所在研究中心锅炉房 4 t/h 燃煤锅炉上, 处理量为 500—1500 m^3/h , 如图 2 所示, 虚线以上为锅炉原有设备, 只有喷钙脱硫反应器为外加的, 为 $400 \times 400 \times 4000 \text{ mm}$ 方形反应器. 处理烟气量由引风机引

入, 与来自加料口的脱硫剂混合, 经喷水加湿后, 与烟气中 SO_2 反应, 强化吸收烟气中 SO_2 , 形成 CaSO_3 和 CaSO_4 颗粒, 经原有的除尘器捕集后排出, 从而完成简易干法烟气脱硫过程.

不同 Ca/S 比条件下进行试验, 获得的结果列于表 1 中.

表 1 不同 Ca/S 条件下 SO_2 去除率测定结果

烟气温度/°C		烟气流 量/ $\text{m}^3 \cdot \text{h}^{-1}$	SO_2 浓度/ $\text{mg} \cdot \text{m}^{-3}$		$\text{Ca}(\text{OH})_2$ / $\text{kg} \cdot \text{h}^{-1}$	水量 / $\text{kg} \cdot \text{h}^{-1}$	Ca/S	SO_2 去除率/%
入口	出口		入口	出口				
120	50	950	2860	1800	2.1	30	0.8	37.0
115	58	950	3290	1950	3.3	25	1.2	40.9
113	59	950	2290	820	3.5	25	1.8	64.4
120	61	950	2430	790	3.9	23	2.3	67.6
110	50	950	1430	370	3.9	30	2.7	74.0

3 结论

(1) 脱硫剂的制备过程中, 添加剂的加入显著地增加脱硫剂的活性及其比表面积. 原料的 CaO 比表面积为 $2.4 \text{ m}^2 \cdot \text{g}^{-1}$, 而加入添加剂后制得的脱硫剂比表面积为 $41 \text{ m}^2 \cdot \text{g}^{-1}$. 增加表比面积即提高其活性.

(2) 脱硫剂平均粒径为 $22.2 \mu\text{m}$, 以细粒为主, 粒径 0—20 μm 占 44.1%; 20—40 μm 占 29.0%, 40—60 μm 占 16.6%; 60—90 μm 占 13.3%.

(3) 高效多孔细粉脱硫剂与 SO_2 反应过程中, 烟气中相对湿度、 SO_2 浓度, 反应温度和脱硫剂比表面积是影响 $\text{Ca}(\text{OH})_2$ 转化率的主要因素.

(4) 中试过程中, Ca/S 摩尔比为 1.5—1.8 时, SO_2 去除率在 60%—70%, 具有较强工业

化应用前景.

(5) 本方法控制 SO_2 排放, 简易、低投资、低成本, 工厂有能力接受运行.

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Assessment of Critical Loads for Acid Deposition in Liuzhou Area. Xie Shaodong, Hao Jiming et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 1—4

In order to provide a quantitative evidence for establishing the target load, acidification processes of soils in Liuzhou area under different acid depositions levels were simulated using a revised MAGIC model on the basis of data about the physic-chemical properties of red earth, the surface water, and the background and present situation of precipitation, which were obtained by field investigations and experiments. The results showed that the soils in Liuzhou area have been already acidified and the acidification trend of the soils will become more serious with time. The upper soil layer is more sensitive to acid deposition while the bottom layer and surface water have larger buffer capacity. Critical loads of potential acidity for different red earth in this area are determined as $0.6—3.8 \text{ keq} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$, and that of sulfur deposition $0.7—3.2 \text{ g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$. In order to protect 95% of soil area from acidic deposition, sulfur deposition should be cut down by 70% of the present level at least.

Key words: critical load, acid deposition, red earth.

Preparation of Polysulfone Hollow Fiber Ultrafiltration Membrane with High Permeability. Jiang Chengzhang et al. (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 5—7

A kind of originally created unique ternary additive of spinning solution and corresponding dry-jet wet-spinning membrane fabricating conditions were invented. The hollow fiber ultrafiltration membrane developed has high permeability, no defect, narrow differential pore size distribution and excellent retentivity. The membrane have double-row finger-like pore support layer structure and have skins both on the inner surface and on the outer surface, so the hollow fiber membrane can be operated under inside pressure or outside pressure. A series of hollow fiber ultrafiltration membranes with molecular weight cut-off of 10000; 30000; 50000 and 100000 respectively.

Key words: polysulfone, hollow fiber, ultrafiltration membrane, preparation.

Study on Biodegradability of Benzene Homolog Compounds by Mixed Bacteria from petrochemical Wastewater Treatment Plant. Wang Jusi, Zhao Lihui et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Envi-*

ron. Sci., 17(5), 1996, pp. 8—12

This paper reported the biodegradability of benzene, toluene, ethylbenzene, o-, m- and p-xylene by mixed bacteria, which were enriched from activated sludge of petrochemical wastewater treatment plant, under aerobic condition. When the concentration of the tested compounds were 50—140 mg/L, the six tested compounds can be biodegrade. Seventeen bacteria strains were sifted from the mixed bacteria, they can biodegrade toluene, ethylbenzene, trimethylbenzene, o-, m- and p-xylene. The ratio of o- and m-xylene were 100% by sifting bacteria. The results indicated that the biodegradability of the compounds strongly depends on its chemical component and structure. At the test system, the biodegradable order of the six tested compounds was: toluene, p-xylene, m-xylene, ethylbenzene, benzene and o-xylene. The intermediates of toluene degraded were detected and was pathway for toluene degraded at aerobic condition.

Key words: biodegradability, benzene, toluene, ethylbenzene, activaty sludge, wastewater treatment.

Development of Simple and Dry Gas Desulfurization Process. Dixin Shen and Guangbin Liu. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 13—15

A simple and economical control technology of sulfur dioxide from the coal-fired boilers using activation calcium hydroxide injection has been developed. The activation calcium hydroxide as a sorbent was prepared by hydrolytic method. The specific surface area of sorbent was $41 \text{ m}^2 \cdot \text{g}^{-1}$, while particles size distribution region 0—10 μm accounted for 24.0%, 10—20 μm for 20.1%, 20—40 μm for 29.0%, 40—60 μm for 16.6% and 60—90 μm for 10.3%. Factors influencing the reaction of sorbent with SO_2 were studied by using a sand-bed reactor in a bench-scale. Preliminary pilot scale test results showed that flow rate gas was $1000 \text{ m}^3 \cdot \text{h}^{-1}$, the concentration of SO_2 was $1430 \text{ mg} \cdot \text{m}^{-3}$ — $4290 \text{ mg} \cdot \text{m}^{-3}$, Ca/S was 1.5—1.8 and SO_2 removal was 60%—70%. The purpose was to develop a FGD technology of low capital and low operating costs to control the SO_2 emission in China.

Key words: sorbents, flue gas desulfurization, pilot scale test.

Experimental Study on Flue Gas Desulfurization with Duct Slurry Injection. Lu Yongqi and Hao Jiming (Dept. of Eviron. Eng., Tsinghua Univ., Beijing 100084), Hou Dongqi and Yu Ronghua (Harbin Power