

煤流化床气化的床内脱硫研究*

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摘要 在 $\phi 100$ mm 加压流化床气化装置上, 进行了义马、大同、夏庄和南定4种煤及2种钙基脱硫剂的床内脱硫试验。结果表明, 所选石灰石和白云石做为床内脱硫剂是可行的, 脱硫率随Ca/S摩尔比增加而提高, 比为3达最大值。操作压力对脱硫率的影响与床层温度和 CO_2 分压有关, 反应处于脱硫剂煅烧区脱硫率不受压力影响, 在非煅烧区脱硫率随压力提高而降低。原煤中全硫含量增加脱硫效率提高。本试验范围所得脱硫率为50%—85%。

关键词 流化床气化, 床内脱硫, 脱硫剂。

气化过程高温脱硫包括床内脱硫和炉外热煤气脱硫, 床内脱硫是将脱硫剂直接加入气化炉内, 在煤炭气化的同时将煤气中的硫化物大部分转化成CaS等, 然后随炉渣排出, 由此减少了煤气中硫化物含量。目前该技术主要用在流化床和气流床气化炉上^[1-4], 本文介绍在煤化所 $\phi 100$ mm 加压流化床气化炉上的试验结果。

1 试验部分

1.1 试验装置

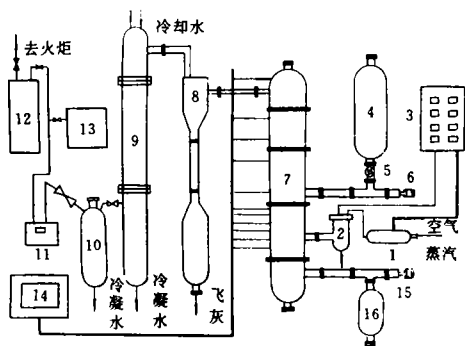


图1 $\phi 100$ mm 加压流化床气化试验装置流程图

1. 1[#] 过热器 2. 2[#] 过热器 3. 温度控制器 4. 加煤斗 5. 星形加料器 6. 给煤螺旋 7. 气化炉 8. 旋风除尘器 9. 间冷器 10. 冷凝液贮罐 11. 煤气流量计 12. 脱硫装置 13. 煤气分析仪 14. 自动记录仪 15. 出灰螺旋 16. 灰斗

图1为流化床试验装置流程图。气化炉气化段 $\phi 100$ mm, 顶部扩大为 $\phi 170$ mm。煤气中 H_2S 由北分厂2305型色谱仪分析, COS和 CS_2 由西南化工研究院生产的WLSP852微量硫测定仪分析, 煤气成分由PE Sigma-2000色谱仪分析。

1.2 试验原料

表1为煤质分析数据。

表1 煤样的分析数据(W/W, %)

煤样	M_{ad}	A_{ad}	V_{ad}	S_{lad}	S_{oad}
义马	11.18	10.08	32.20	2.09	1.47
大同	2.02	7.26	26.22	1.04	0.60
夏庄	0.77	10.10	9.97	3.66	1.11
南定	3.79	9.48	5.41	3.53	1.41

选尚乐白云石和寨口石灰石为试验用脱硫剂, 表2为分析数据。

表2 脱硫剂分析数据(W/W, %)

样 品	CaO	MgO	S_{lad}
寨口石灰石	45.08		<0.01
尚乐白云石	26.60	20.72	0

2 试验结果及讨论

试验入炉煤粒度0.2—1 mm, 脱硫剂采用

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按 Ca/S 摩尔比与煤预混的方式加入气化炉内。床内脱硫效率用下式计算：

$$\eta = \left(1 - \frac{G_g}{G_c + G_s} \right) \times 100\% \tag{1}$$

式中， η 为脱硫率(%)， G_g 为单位时间所产煤气中含硫总量(g/h)， G_c 为单位时间入炉煤中含硫总量(g/h)， G_s 为入炉脱硫剂中含硫量(g/h)。

2.1 脱硫剂粒度对脱硫率的影响

表 3 为义马煤加不同粒度白云石的气化试验结果。可见 0.15—0.6 mm 粒度范围内脱硫率稍高，表明存在一相对较佳的脱硫剂粒度范围。脱硫剂粒度对脱硫率的影响表现在 2 个方面：一是脱硫剂粒度大，其比表面积相对较少，且因脱硫剂密度大于煤(焦)，易沉入床层底部，不利于脱硫反应进行，但粒度大的脱硫剂夹带损失小，在床层内停留时间长，又有利于脱硫反应。二是脱硫剂粒度小，其比表面积大，Borgwardt^[5]曾研究比表面积对 CaO 和 H₂S 反应的影响，发现比表面积大则反应速率快，且粒度小易均匀分布在床层中，与硫化物接触机会大，也有利于气固相间传质传热，从而加快脱硫反应速率。然而脱硫剂粒度下限要受到流化速度限制，粒度越小，被夹带出去的量越大，脱硫剂损失大又不利于脱硫反应进行。几种因素相互作用的结果便会有一相对较好的脱硫剂粒度存在。本试验脱硫剂粒度均选 0.15—0.6 mm。

表 3 脱硫剂粒度对脱硫效率的影响

脱硫剂粒度(mm)	0.15—0.6	0.6—0.1	0.15—1.0
脱硫率(%)	72.8	68.5	70.0

2.2 Ca/S 比值对脱硫率的影响

表 4 为改变白云石 Ca/S 比对义马煤和南定煤气化时床内脱硫效率的影响。可见二者有相似的规律，开始脱硫率随 Ca/S 比增加而提高，到 Ca/S 比为 3 时达到最高点，而后不再增加。

Abbasian^[6]用公式：

$$r = K[H_2S][CaO] \tag{2}$$

来描述石灰石或白云石与 H₂S 反应速率，Borg-

wardt^[7]给出了类似的表达式，不过其反应物为 CaCO₃。对比本试验，提高 Ca/S 比，就提高了床层中 CaO 或 CaCO₃ 浓度，从而加快脱硫反应速率，在同等条件下提高了床内脱硫效率。但表 4 的数据同时表明 Ca/S 比达到 3 后，脱硫率不再增加，因此，再增加脱硫剂是不必要的。

表 4 Ca/S 比对脱硫率的影响

Ca/S (mol/mol)	1.0	2.0	3.0	4.0
义马 η (%)	50.3	67.1	73.0	71.8
南定 η (%)	55.2	73.5	78.2	76.1

2.3 操作压力对脱硫率的影响

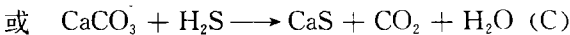
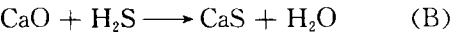
表 5 给出义马和南定煤以石灰石 Ca/S 比为 3，床层温度分别为 920℃、960℃时操作压力对脱硫率的影响。可见压力低时操作压力提高对 2 种煤的脱硫率影响不大，达一定值后再提高则脱硫率下降。

表 5 操作压力对脱硫率的影响

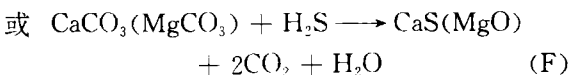
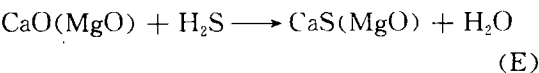
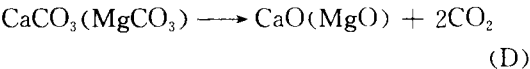
压力(MPa)	0.1	0.75	1.5	2.0
义马 η (%)	75.2	75.7	73.1	70.5
南定 η (%)	84.0	84.4	84.1	80.2

气化炉运行时，床层处于还原性气氛中，煤中大部分硫转化成 H₂S，小部分转化成 COS 和 CS₂ 等，脱硫剂加入后与硫化物反应，公认的脱硫反应有(以 H₂S 为例)：

脱硫剂为石灰石时：



脱硫剂为白云石时：



从反应式看，(B)、(E)为脱硫剂处于煅烧区的反应，其反应平衡与压力无关；(C)、(F)为非煅烧区的反应，其平衡受温度和压力(CO₂ 分压)影响。2 种反应的主要区别是脱硫剂中的

CaCO_3 是否分解, 即钙以那种形式参加脱硫反应, 而 CaCO_3 分解与否与操作温度及炉内 CO_2 分压有关。Squires^[8] 用(3)式确定 CaCO_3 分解时(即(A)式)的 CO_2 平衡分压。

$$\lg(P_{\text{CO}_2}) = -8799.7/T_K + 7.521 \quad (3)$$

式中 P_{CO_2} 为床层内 CO_2 分压 atm, T_K 为反应温度(K)。

将试验数据与由(3)式求得的 CO_2 平衡分压对比, 发现义马煤 0.1、0.75 MPa 压力操作

点和南定煤 0.1、0.75、1.5 MPa 3 个操作点均处于 CO_2 分压低于对应温度时 CO_2 平衡分压, 说明脱硫反应处于脱硫剂煅烧区, 按(B)式反应, 操作压力改变对反应影响少, 脱硫率变化不大。其余点处于脱硫剂非煅烧区, 即反应按(C)式进行, 此时提高压力不利于脱硫反应进行, 因而导致脱硫率下降。因此在温度一定时, 操作压力对脱硫效率的影响主要是通过床层内 CO_2 分压来决定。文献[3]得出相似结论。

表 6 脱硫试验结果

参 数	义 马		大 同		夏 庄		南 定	
	白云石	石灰石	白云石	石灰石	白云石	石灰石	白云石	石灰石
Ca/S (mol/mol)	3	3	5	5	3	3	3	3
操作压力(MPa)	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
床层温度(°C)	920	920	980	980	970	985	960	960
脱硫率 η (%)	74.18	75.7	49.9	56.8	83.14	83.88	80.19	84.4

2.4 脱硫剂和煤质对脱硫率的影响

表 6 给出 4 种煤与 2 种脱硫剂分别气化时的典型试验结果。

可见 2 种脱硫剂白云石和石灰石均能脱除气化过程中产生的硫化物, 并获得较高的床内脱硫效率。对比表 1 和表 6 等, 不同煤种气化时床内脱硫率高低与原煤样中全硫含量有关, 而与煤中有机硫和无机硫所占比例关系不大, 即原煤中含硫量高, 其气化时得到的床内脱硫率高, 反之亦然。

原煤中全硫含量高, 在气化过程中转化成的 H_2S 和 COS 浓度高, 从式(2)和 2.3 中脱硫反应式看, $\text{H}_2\text{S}(\text{COS})$ 浓度高, 脱硫反应速度加快, 且反应有利于向脱硫方向进行。在一定温度和压力下, 床层中 $\text{H}_2\text{S}(\text{COS})$ 最低浓度理论值为脱硫反应达平衡时的 $\text{H}_2\text{S}(\text{COS})$ 值。从试验结果看, 除大同煤出炉煤气所含 H_2S 约 910 mg/ m^3 稍低外, 其余 3 种煤出炉煤气中 H_2S 含量为 1290—1590 mg/ m^3 , 相差不很大。相对来说, 高硫煤气化时产生的硫化物被脱硫剂缚住(转化成 CaS)的数量大, 亦即脱硫率高。

本试验获得脱硫率为 50%—85%, 出炉煤气中 H_2S 含量尚过高, 因而进一步提高床内脱硫效率和钙利用率值得深入研究。

3 小结

(1) 脱硫效率随 Ca/S 摩尔比增加而提高, 到 Ca/S 比为 3 时达最大值。

(2) 操作压力对脱硫率的影响是通过气化炉床层内 CO_2 分压和温度决定。如反应处在脱硫剂煅烧区, 压力变化对脱硫率无影响, 处于非煅烧区则脱硫率随压力提高而降低。

(3) 石灰石和白云石均能脱除煤中硫。脱硫率随煤中全硫含量增加而提高, 从 50% 到 85%。

致谢 本试验得到谢可玉、逢进两位专家的帮助, 沙兴中教授提出宝贵意见, 季士清、王志斌、张迪、王玉峰等人参加了试验工作, 在此谨表谢意。

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tration increased; and the toxicity (EC₅₀, 96 h.) of rare-earth elements on *Chlorella pyrenoides* was in sequence as: Nd > Ce > Pr > La > mixture of them, but little difference.

Key words: rare-earth element, *Chlorella pyrenoides*, effect on growth and reproduction.

Study on in-Bed Desulfurization within Fluidized Bed Coal Gasifier. Bu Xuepeng et al. (Beijing Research Institute of Coal Chemistry, Central Coal Mining Research Institute, Beijing 100013); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 39–41

The data obtained from the tests indicated that both limestone and dolomite can be used effectively for capturing sulfur during the gasification of high sulfur coals. Desulfurization efficiencies can be improved with increasing the Ca/S molar ratio, the efficiencies were maximum when the ratio was 3, or by increasing total sulfur in raw coals. The effect of operating pressure on desulfurization efficiency is determined by temperature and partial pressure of carbon dioxide. The desulfurization rate was range of 50%–85% under different conditions.

Key words: fluidized bed gasification, in-bed desulfurization, desulfurization sorbent.

Mass Transfer-Reaction Process Mechanism of Wet Flue Gas Desulfurization with Lime. Wu Zhongbiao and Tan Tian'en (Dept. of Chem. Eng., Zhejiang University, Hangzhou 310027); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 42–44

By studying experimentally wet flue gas desulfurization with lime as absorbent and rotating-stream-tray scrubber as absorber, the mass transfer and reaction process on Ca(OH)₂ slurry absorbing SO₂ is analyzed. Furthermore, the process mechanism is proposed. According to the mechanism, the total reaction rate is controlled by SO₂ diffusion in gas phase and Ca(OH)₂ dissolution and diffusion in liquid phase. The reaction process can be divided into three stages, the stage controlled by gas phase resistance, by gas phase and liquid phase resistance, and by liquid phase resistance. The process mechanism has been verified by the experiment. These results will help to optimize the design and operation of the industrial installation of wet flue gas desulfurization with lime.

Key words: flue gas desulfurization, mechanism, mass transfer-reaction process, lime, wet.

Effects of Three Sorts of Anaerobic Promoter on Anaerobic Digestion of the Waste Liquor from Ammonium Sulfite Pulping of Straws. Zhang Renquan (Dept. of Resource and Environ. Sci., Hefei Univ. of Technol., Hefei 230009); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 45–46

The effects of activated carbon, ferrous sulphate and bentonite on anaerobic digestion of the waste liquor from ammonium sulfite pulping of straws have been analysed on the basis of the experimental results of anaerobic batch assays with the waste liquor. The results indicate that, with a dose of 2.5 g/L, each sort of the anaerobic promoter can substantially promote anaerobic digestion of the waste liquor, which can increase 30 day total gas production of the anaerobic system by 16.1%, 13.9% and 26.1% respectively compared with the control. The ac-

tion mechanisms of the three sorts of anaerobic promoter have been discussed preliminarily.

Key words: anaerobic promoter, waste liquor from ammonium sulfite pulping of straws, anaerobic digestion, action mechanisms.

Using Hydra Reaggregations Evaluating the Safety of Two Kinds of Food Additives. Cheng Qinyao et al. (Dept. of Biology, Anhui University, Hefei 230039); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 47–48

This paper studied the safety of two kinds of food additives using *Hydra* reaggregations. The results showed that both sodium benzoate and sodium nitrite inhibited the growth of reaggregations. The minimum effective concentrations were 34.7×10^{-4} mol/L and 2.9×10^{-3} mol/L respectively. In addition, the negative correlation existed between the depolymerization time of the reaggregations and the concentration of food additives. Therefore, *Hydra* reaggregations technique will be a rapid screening method for predicting the potential toxicity of food additives.

Key words: *Hydra* reaggregation, food additive, evaluation safety, rapid screening.

A Study on Long-wave Pulsed Electromagnetic Fields Around A Long Range Navigation Station. Yao Gengdong et al. (School of Public Health, Zhejiang Medical University, Hangzhou 310031); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 49–50

A measurement and a theoretical calculation of long-wave pulsed electromagnetic fields (PEMF) around the antenna of the first long range navigation station in China were conducted. The results showed that the electric field intensities were 0.5–3.6 V/m (RMS) corresponding to peak values of 38.5–276.9 V/m in the PEMF generating room; in the residential area which is 850–1100 m away from the antenna, the electric fields were 0.7–3.9 V/m corresponding to peak values of 53.9–300.3 V/m; the PEMF decreased in environment with the distance away from the antenna and when the distance is over 1200 m from it, the fields tended towards minimum.

Key words: pulse, long-wave, environment, electric field intensity.

Determination of Hydraulic Load Cycle in Rapid Infiltration Treatment System of Waste Water. Wu Yongfeng et al. (Dept. of Environ. Sci., China University of Geosciences, Beijing, 100083); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 51–53

Hydraulic load cycle is the most important operation parameter in rapid infiltration treatment system of waste water. The decrease curve and recovery curve of infiltration rate in flooding and drying periods are obtained from the in situ test with the area of 80 m² and flooded with brewery waste water. The curves can be expressed with exponential and logarithmic equations respectively. A quantitative method is proposed to determine the hydraulic load cycle with maximum hydraulic load. The calculated result is 1.78 days flooding and 2.77 days drying, very similar with the test results.

Key words: rapid infiltration, hydraulic load, hydraulic load cycle, infiltration rate.

A New Way to Accelerate the Start-up of UASB Reactor