

Fe-Si 添加剂对型煤燃烧固硫的促进作用*

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摘要 为提高型煤燃烧固硫效率, 用微量 Fe-Si 氧化物作为固硫促进剂加入钙碱吸收剂中, 经 1200℃ 以上高温燃烧后进行固硫率计算, 其固硫率可达 65%。对炉渣产物用 X 射线粉末衍射法进行物相鉴定, 发现生成一种热稳定化合物 $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$, 实验证明其有利于型煤燃烧固硫率的提高。

关键词 型煤, 固硫, X 射线粉末衍射。

为减少煤燃烧时 SO_2 的排放, 通常用一种廉价的钙碱吸收剂加入型煤中使 SO_2 转化为硫酸钙而固定在炉渣中^[1]。但硫酸钙不是耐高温相, 由于燃烧过程中炉温较高, 超过 800℃ 以后所形成的硫酸钙则开始分解, SO_2 将再次逸出影响固硫效果^[2]。本实验用微量 Fe-Si 氧化物作为固硫促进剂加入到钙碱吸收剂中, 经 1200℃ 以上高温燃烧并对炉渣产物用 X 射线粉末衍射 (XRPD) 进行物相鉴定, 发现形成一种热稳定化合物 $\text{CaFe}_3(\text{SiO}_4)_2\text{OH}$, 基覆盖或包裹硫酸钙晶粒, 延缓并阻止硫酸钙的分解, 促进固硫率的提高。

1 实验部分

1.1 原料试剂

高硫煤: 四川重庆烟煤。煤质分析: C^f : 67.49%, A^f : 21.38%, V^f : 9.61%, S^f : 2.05%, H^f : 2.77%, N^f : 1.19%。钙、铁、硅等氧化物均为化学纯试剂, 北京化工厂生产。

1.2 样品的制备

定量称取已烘干的煤粉于研钵中, 按钙硫比为 2 定量加入固硫剂 CaO 及适量添加剂氧化铁、 SiO_2 , 充分研磨后盛入瓷舟, 置于管式电炉中燃烧, 打开温度控制系统、 SO_2 分析仪及记录仪, 缓慢地加热达 1200℃ 并维持恒温 0.5 h, 空气流量约 5 L/min。实验装置如图 1 所示。

1.3 分析与表征

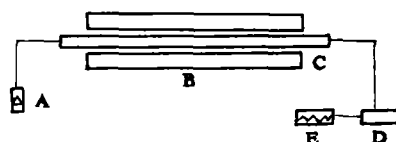


图 1 实验装置

A. 空气流量计 B. 管式电炉 C. 反应管
D. SO_2 测定仪 E. 记录仪

利用脉冲-荧光二氧化硫分析仪 (热电公司 40 型) 进行 SO_2 分析, 并用 X 射线粉末衍射仪 (丹东仪器厂 Y-2 型) 对经 1200℃ 以上高温燃烧后的炉渣作物相鉴定, 根据原煤硫含量与型煤燃烧过程中 SO_2 释放浓度计算固硫率, 其结果列于表 1。

表 1 添加剂对固硫率的影响¹⁾

样品	吸收剂	促进剂	固硫率 ²⁾
1			0.232
2	CaO		0.459
3	CaO	Fe_2O_3	0.483
4	CaO	SiO_2	0.576
5	CaO	$\text{Fe}_2\text{O}_3 + \text{SiO}_2$	0.650

1) 煤粉来源于重庆烟煤 2) 按原煤 S 含量与 SO_2 浓度计算

从表 1 可以看出, SiO_2 作为一种促进剂加入 (样品 4) 有助于固硫, 而仅仅加入 Fe_2O_3 (样品 3) 没有明显的固硫效率, 当铁-硅氧化物同时加入 (样品 5) 则有最佳的固硫效率, 对其固硫率可达 65%。

对煤粉加入吸收剂与促进剂后的燃烧产物

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用 X 射线粉末衍射法进行物相鉴定, 其结果列于表 2.

表 2 型煤燃烧产物的 XRPD 物相鉴定

样品	燃烧产物的物相组成
1	3Al ₂ O ₃ · 2SiO ₂ , α-SiO ₂ , α-Fe ₂ O ₃ , 长石
2	3Al ₂ O ₃ · 2SiO ₂ , α-SiO ₂ , α-Fe ₂ O ₃ , CaSO ₄ , 长石
3	3Al ₂ O ₃ · 2SiO ₂ , α-SiO ₂ , α-Fe ₂ O ₃ , CaSO ₄ , 长石
4	3Al ₂ O ₃ · 2SiO ₂ , α-SiO ₂ , α-Fe ₂ O ₃ , CaSO ₄ , 长石
5	3Al ₂ O ₃ · 2SiO ₂ , α-SiO ₂ , α-Fe ₂ O ₃ , CaSO ₄ , 长石 CaFe ₃ (SiO ₄) ₂ OH,

从表 2 中所列燃烧产物的物相组成结果可知, 除在原煤直接燃烧的 1 号样品灰渣中未检出固硫相硫酸钙, 其余样品的产物中均见有硫酸钙. 此外在加入铁-硅氧化物的 5 号样品灰渣中, 发现除保存有大量硫酸钙外, 并有热稳定相 CaFe₃(SiO₄)₂OH 存在(见图 2), 这种耐高温的硅酸盐相在其余样品的渣中则未见到.

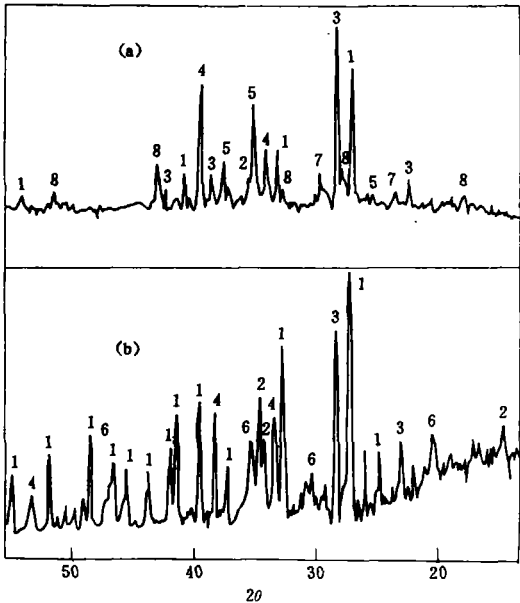


图 2 2 个典型炉渣样品的 XRPD 谱图
(a) 具有 Ca-Fe-Si 添加剂的型煤样品 (b) 模拟样品
1. CaSO₄ 2. CaFe₃(SiO₄)₂OH 3. SiO₂ 4. CaO
5. Fe₂O₃ 6. Ca(OH)₂ 7. 长石 8. 3Al₂O₃ · 2SiO₂

片^[3]进行对照分析, 证实产物中除有硫酸钙等物相外, 并生成一种新的耐热物相 CaFe₃(SiO₄)₂OH, 其粉晶衍射数据分析见表 3.

表 3 CaFe₃(SiO₄)₂OH 的粉晶衍射数据

产品产物 的主要谱线		JCPDS 卡片: 25-149 CaFe ₃ (SiO ₄) ₂ OH	
d/Å	I/I ₁	I/I ₁	d/Å
7.308	60	7.305	70
3.258	50	3.255	55
2.850	90	2.849	95
2.710	75	2.714	70
2.680	100	2.678	100

图 2 是 2 个典型炉渣样品的 XRPD 谱图: 图 2(a)具有 Ca-Fe-Si 添加剂的型煤样品, 图 2(b)模拟样品, 从 XRPD 谱图中可以见到在型煤样品的炉渣中具有耐高温相 CaFe₃(SiO₄)₂OH, 同时硫酸钙大量保存于炉渣产物中, 但未发现其它固硫物相. ESCA 分析结果指出 S 的价态除 SO₄²⁻ 之外, 无其它价态. 另外根据扫描电镜的观察结果, 表明在该体系的炉渣产物中, Fe、Si 组分与 CaSO₄ 晶体有着依附关系, 紧密共生, 并附于其表面上^[4], 说明由于 Ca-Fe-Si 氧化物的加入形成一种耐热硅酸盐稳定相 CaFe₃(SiO₄)₂OH, 由于其覆盖或可能包裹 CaSO₄ 晶粒, 延缓与阻止了 CaSO₄ 的分解, 使其分解温度升高而提高了固硫率, 这阐明了新的固硫作用机理, 对于今后改进型煤工艺配方有一定指导意义.

3 结论

煤中适当加入铁、硅氧化物添加剂, 经高温燃烧未形成新固硫物相, 实验证明生成耐热硅酸盐稳定相 CaFe₃(SiO₄)₂OH, 其覆盖或包裹硫酸钙晶体, 延缓与阻止它分解, 使固硫率明显提高, 这种新的固硫作用机理对改进型煤工业配方有一定指导意义.

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2 结果与讨论

为了模拟煤燃烧的实际条件, 按一定比例加入 CaO, SiO₂, S, Fe₂O₃ 及 FeS 制备样品, 缓慢地加热到 1200℃ 恒温 0.5 h, 燃烧后的灰渣产物用 XRPD 作物相鉴定, 并与 JCPDS 数据卡

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., $\eta = 1 - [(T_i - T_w)/(T_0 - T_w)]^{-\frac{\alpha}{\beta - \alpha}}$, 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 CaFe₃(SiO₄)₂OH 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.