

型煤高温固硫终产物 Ca-Fe-S-Si-O 体系的表征*

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摘要 当型煤中适当加入添加剂硅、铁组分燃烧生成新的 Ca-Fe-S-Si-O 体系后, 固硫率明显提高。本文用 X 射线粉末衍射法与 X 射线荧光光谱法对该体系的高温固硫终产物进行表征, 分析了灰渣样品并讨论添加剂对固硫率的影响, 为型煤工业配料寻求可靠依据。

关键词 型煤, 固硫, X 射线粉末衍射, X 射线荧光光谱分析。

为降低燃煤中二氧化硫排放问题, 目前通常采用一些脱硫措施, 如在煤中加入钙系化合物作为固硫剂制成型煤, 燃烧生成硫酸钙, 使硫固定在炉渣内^[1], 但硫酸钙不是耐高温相, 通常在炉温超过 800℃ 以后, 因产生分解作用, 二氧化硫将再次逸出, 影响固硫效果^[2], 当在煤中加入含 Sr 添加剂燃烧时, 则发现生成耐热物相—— $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ ^[3], 对固硫率有所提高, 但实验表明该体系的固硫效率并不十分理想, 因此有必要在此基础上作进一步的改进。本研究通过实验证明在煤中适当加入添加剂 Si、Fe 组分燃烧生成新的 Ca-Fe-S-Si-O 体系后, 固硫率明显提高, 并采用 X 射线粉末衍射法与 X 射线荧光光谱法对该体系中的高温固硫终产物进行表征; 分析了灰渣样品, 在此基础上讨论添加剂对固硫率的影响, 为型煤工业配料寻求可靠依据。

1 实验部分

1.1 原料试剂

高硫煤: 四川重庆天府烟煤。

煤质分析: C^f : 54.94% A^f : 34.00% V^f : 15.85% S^f : 3.53% Q^f : 22.45MJ H^f : 3.29% N^f : 0.93%。

钙、铁、硅等氧化物均为化学纯试剂, 北京化工厂生产。

1.2 灰渣样品的制备

定量称取已烘干的煤粉于研钵中按钙硫比

为 2 定量加入固硫剂氧化钙及适量添加剂氧化铁、二氧化硅, 充分研磨后盛入瓷舟, 置于管式电炉中燃烧, 经 1200℃ 以上高温燃烧后将所获得的灰渣样品封存待分析。实验装置如图 1 所示。

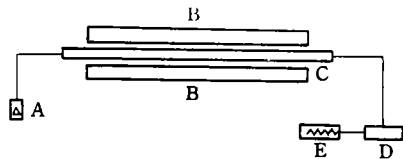


图 1 实验装置

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

1.3 X 射线粉末衍射分析

X 射线粉末衍射可在结晶物质的结构研究方面提供重要的资料, 是物相鉴定的有效手段之一。本实验采用 X 射线衍射仪法, 该方法使用测角仪和一套射线探测系统, 直接测量记录衍射线的位置和强度。将灰渣样品经充分研磨后, 用无水乙醇均匀分散在平面玻璃样品板上, 在 Y-2 型 X 射线衍射仪(丹东仪器厂制造)上进行 XRPD 分析。分析结果见图 2 和图 3。实验条件: 铜靶辐射, 镍片滤波, 管压 30kV, 管流 15mA, 发射狭缝 1°, 散射狭缝 1°, 接收狭缝 0.2mm, 扫描速度 2°/min, 纸速 20mm/min, 时间常数 1s, 用正比计数管探测(道宽 1.1V, 基线 3.6V)。

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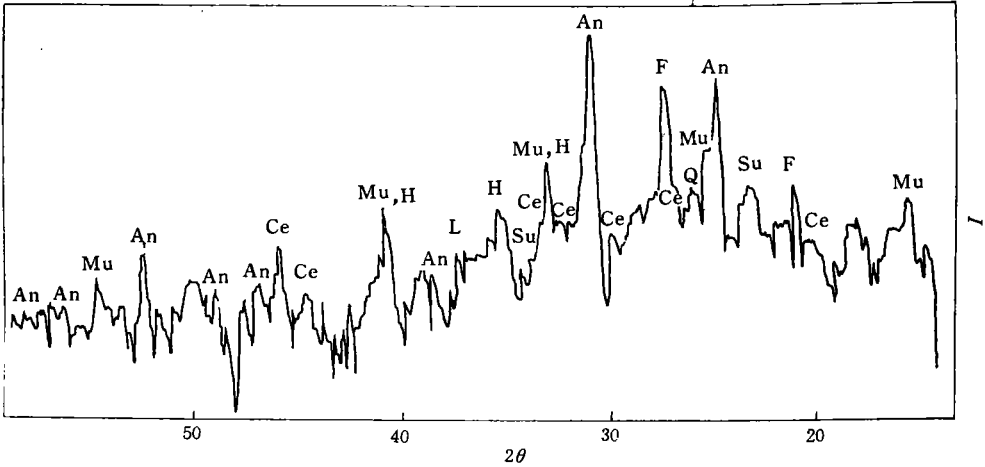


图 2 Sr 体系灰渣样品的 XRPD 图谱

An;CaSO₄ Mu;2Al₂O₃·3SiO₂ H;α-Fe₂O₃ Su;SrSO₄ L;CaO Ce;3CaO·3Al₂O₃·CaSO₄ Q;SiO₂ F;长石

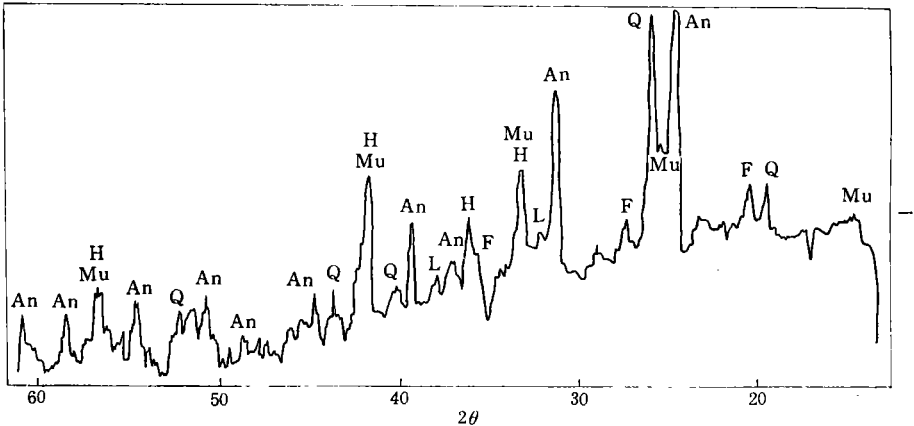


图 3 Si、Fe 体系灰渣样品的 XRPD 图谱

An;CaSO₄ Mu;2Al₂O₃·3SiO₂ H;α-Fe₂O₃ L;CaO Q;SiO₂ F;长石

1.4 X 射线荧光光谱分析

为了确定该体系的最终固硫效率,对灰渣样品进行 X 射线荧光光谱(XRFA)分析,测定样品中硫含量,标准样品的制备是选用某已知硫量的土壤分别加入 0.5%—10%不同含量的硫,充分研磨并混匀,各称取 10mg,均匀涂抹在 φ30mm 胶带上,待测灰渣样品则是直接称取 10mg 涂在 φ30mm 胶带上,用日本理学 3070E 型全自动 X 射线荧光光谱仪,铑靶 X 射线管进行测定,测定条件见表 1,分析结果见表 2。

表 1 X 射线荧光光谱分析测定条件

分析元素	硫
分析线(2θ)	111.25°
背景(2θ)	112.60°
管压 kV/管流(mA)	50/40
分光晶体	Ge
PHA ¹⁾	100—350
探测器	P-Fc 气流正比计数器
峰值计数时间(s)	40
背景计数时间(s)	20
光路	真空

1) PHA——脉冲高度分析器

表 2 灰渣中硫的 XRFA 测定结果(重量%)

样 品	煤加固硫剂与不同添加剂后的燃烧灰渣	
固硫剂	CaO	
添加剂组分	Sr	Si, Fe
S 含量	3.99	7.33
固硫率(%) ¹⁾	51	93

1) 按原煤中的灰分量 34.00% 与硫含量 3.53% 计算

2 结果与讨论

当煤中适量加入不同添加剂组分锶、硅、铁经 1200℃ 以上高温燃烧后,对其灰渣样品作了 X 射线粉末衍射分析,结果表明样品中的物相组成有明显差异;图 2、图 3 分别为加 Sr 与 Si、Fe 所形成的 2 种不同体系的 X 射线结构状态分析结果,从谱图中可以见到在 Sr 体系中, CaSO_4 大部分已分解,生成新的以复盐形式出现的耐热物相 $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ ^[4] 以及 SrSO_4 ,而在 Si、Fe 体系中, CaSO_4 大部分未经分解仍保留在灰渣中,但未见复盐这种耐热物相存在。

另外对灰渣样品同时进行了 X 射线荧光光谱分析,作了硫在灰渣中的含量测定(表 2),可知 2 种不同添加剂体系的灰渣样品中,其含硫量也有显著差异,分别为 3.99% 与 7.33%,并以原煤中所含有的灰分 34.00% 与硫含量 3.55% 进行计算(见煤质分析结果),其固硫率分别为 51% 与 93%,这表明当煤中添加剂组分由 Si、Fe 取代 Sr 之后,固硫率则大为提高。

综上所述,2 种不同体系的终产物其固硫率有着明显差异,并从灰渣样品的物相组成结果来看,在 Si、Fe 体系中并未形成固硫新物相。另外

在 XRPD 图谱中,明显可见添加剂 SiO_2 与 Fe_2O_3 的特征峰大大增强,说明这 2 种组分未参与任何化学反应,只是起到缓解或阻止硫酸钙分解的作用,同时根据扫描电镜的观察结果,表明在该体系的灰渣样品中, Si、Fe 组分是与硫酸钙晶体有着依附关系,紧密共生,并附于其表面上,由此而引起 CaSO_4 分解温度后延,这说明 Si、Fe 组分虽未参与任何化学反应,却起到了阻止 CaSO_4 分解的作用,使其能大量保留下来,因此大大提高了该体系的固硫率,这种固硫特征与 Sr 体系有着根本上的区别,也是在固硫机理研究中一项新的进展,这对于今后改进型煤工艺配方有一定指导意义,在工业型煤的发展与开发中有广泛的应用前景。

3 结论

(1)通过对 Si、Fe 体系的型煤高温固硫终产物的表征,指出该体系的固硫效果极好,其固硫率高达 93%。

(2)实验结果表明加入的 Si、Fe 添加剂组分未形成新的固硫物相,只是起到缓解与阻止硫酸钙分解的作用,使其能大量留在灰渣中,而提高了固硫率。对于今后改进型煤工艺配方有一定指导意义。

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• 环境信息 •

热带地区可能难以恢复原状

据史密森热带研究所的一份研究报告称,热带地区可能难以从重大的漏油事故的影响中恢复过来。该所研究人员已对 1986 年在巴拿马拉斯米纳湾加勒比沿海的一次漏油进行了监测。在那次漏油事件中,多达 10 万桶原油漏进靠近海岸线的、拥有红树林、海草床和珊瑚礁的海域。该海域曾包括史密森研究所的加勒塔角海洋站。大约 7% 的红树林被最初的漏油所摧毁,化学分析表明,5

年之后,红树林沉积物仍含有相当新鲜的石油。还存在着 1968 年在这同一海域发生的漏油事故的油的证据。珊瑚礁群落的总生产力已下降,该生态系统种群已转移,例如食肉性鱼类的数量减少。该所研究人员担心:珊瑚种群可能要过一个多世纪才能恢复到漏油前的水平。

小康译自 ES&T, 1994, 28(2):58A

Abstracts

Chinese Journal of Environmental Science

Characteristics in Mutagenicity of the Drinking Water from Representative Areas in China. Xu Fengdan et al. (Institute of Environmental Health Monitoring, CAPM, Beijing 100021); *Chin. J. Environ. Sci.*, **15**(3), 1994, pp. 1—6

The tap waters, raw waters and chlorinated raw waters from the waterworks in Shanghai, Kunming, Harbin, Shengyang, Guangzhou, Wuhan and Shenzhen cities were studied for their characteristics in mutagenicity by using an Ames Test. All the tap waters were found to contain direct mutagens of frameshift, with strain TA98 to be the most sensitive strain for such a monitoring. The chlorinated raw waters from all the cities except for Shenzhen were found to have significantly a stronger mutagenic activity than their raw waters in both strain TA98 and TA100, with and without S9, as evaluated in terms of relative activity by water volume (rev./L) or by weight of water concentrate (rev./mg), particularly in the case of Shanghai. The results provide a scientific basis for selecting representative cities to study the mechanism on the formation of toxic chlorinated organics during chlorination of drinking water.

Key words: drinking water, chlorination, mutagenicity Ames Test.

QSAR Model Parameters Research on Substituted Aromatic Compounds. Wang Lianshen, Liu Zhengtao et al. (Department of Environmental Science, Nanjing University, Nanjing 210008); *Chin. J. Environ. Sci.*, **15**(3), 1994, pp. 7—10

The quantitative structure activity relationships (QSAR) between acute toxicities of 47 substituted aromatic compounds to *Daphnia magna* (48h, EC₅₀/LC₅₀) and seven classical parameters of molecules had been investigated. The biological effects were found to be mainly related to K_{ow} (octanol/water partition coefficient), π_x (hydrophobic bonding effects), $^1X^v$ (substituent molecular connectivity index). The contribution rank of the aromatics in quantitative relationships was: hydrophobicity/hydrophilicity > electronic effects > steric effects.

Key words: aromatic derivative, toxicity effects, parameters analysis, QSAR.

Development of the Technology for Immobilizing Microorganism on a PVA Entrapped Activated Carbon and Its Application to Degradation of Isocarbophos. Chen Ming, Luo Qifang (Institute of Environmental Medicine, Tongji Medical University, Wuhan 430030); *Chin. J. Environ. Sci.*, **15**(3), 1994, pp. 11—14

A technology has been developed for immobilizing microorganism on an activated carbon which has

been entrapped by using polyvinyl alcohol (PVA) as an entrapping agent. The preferable preparation processes were given for such an immobilization. The trial study on application of this technology to degradation of isocarbophos, an organophosphorus pesticide, was conducted. The results show that the immobilized microorganism can be effective in a wider range of temperatures, pH values, and concentrations of isocarbophos in water. During a 3 month period of continuous operation, 55%—72% of the pesticide were removed from water if it had an initial concentration of 1300—2500mg/L by COD_{Cr} in water and was degraded in a thermostatic vibratile table (30°C, 150rpm) for 24 hours (HRT).

Key words: isocarbophos, immobilized microorganism, PVA, activated carbon, organophosphorus pesticides.

Characterization of the Ca-Fe-S-Si-O System as a Final Product of High Temperature Coal Briquet Sulfur Capture. Lin Guozhen, Xiao Peilin et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **15**(3), 1994, pp. 15—17

The ash from burning a coal briquet with an additive (Si, Fe) for sulfur capture was characterized by using a X-ray powder diffraction method and a X-ray fluorescent spectrometry, giving the same chemical composition as that derived from the elemental analysis data. The results also indicated that CaSO₄ was the major constituent of the ash; the content of sulfur in the ash was found to be 7.33% by weight; and the ash had a composition of Ca-Fe-S-Si-O showing a higher rate of sulfur capture.

Key words: coal briquet, sulfur capture, XRPD, XRFA.

Simulating Study on an Artificial Clay Layer Suppressed Movement of Waterborne Salt through the Sediments of Oxidative Ponds in Salinized Areas During Dry Seasons. Wang Hong, Ye Changming, Yin Chengqing (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **15**(3), 1994, pp. 18—21

The modelling studies have been qualitatively carried out on the movement of waterborne salt through different stratified structures of the sediment of oxidative ponds in a salinized Xiaqinghe area during dry seasons by using simulated soil columns in laboratory. The results show that the homogenous earth of original sediment has a high ability to transport water and is prone to allow water to be evaporated, making the waterborne salt to be carried up and largely accumulated on the surface of pond bottom. The maximum suction head to maintain such