Fe_2O_3 对型煤固硫作用的机理探讨

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摘要 根据煤中硫的着火点, 发现硫的固定主要发生在温度低于 500℃的阶段, 升温时间应小于 30min. Fe_2O_3 用量增多, $CaSO_3$ 转化生成 $CaSO_4$ 的量增多; 通过 $CaO+SO_2+0.5O_2 \rightarrow CaSO_4$ 的反应来模拟实际的煤燃烧时硫的固定过程, 发现 Fe_2O_3 的加入对硫的固定起着较大的促进作用, 而且 Fe_2O_3 主要是促进 $CaO+SO_2 \rightarrow CaSO_3$ 这一反应过程.

关键词 型煤, 固硫, 三氧化二硫, 硫酸钙, 氧化钙.

在煤中加入固硫助剂 Fe_2O_3 后, 煤中硫的固定发生了有利的变化[1]. 在 6‰的 Fe_2O_3 重量百分含量时固硫率达到最高. 煤燃烧后灰渣硫主要以 $CaSO_4$ 形式存在. 据此笔者通过采用纯净的 $CaSO_4$ 试剂和不同含量的 Fe_2O_3 混合物在不同温度下的变化考察了 $CaSO_4$ 的分解规律, 发现当 Fe_2O_3 的含量为 4‰时, $CaSO_4$ 的分解率最低. 针对固硫率及其影响因素设计了一系列单因素试验, 以便进一步揭示直接而又实用的规律.

1 固硫反应过程的阶段性

将煤按照最佳配比条件(CaO 与煤中硫的摩尔比为 2, 再以 1kg 干煤粉重量为基准, 按重量比 6‰称取 Fe_2O_3 加入煤粉中) 制成煤球, 晒干, 称取一定量的煤球置于瓷舟中, 放入电炉里加热. 型煤固硫率和温度、恒温时间及升温速度都存在着一定的关系, 为了研究固硫率和升温速度之间的关系, 可以通过调节加在电炉上的电压达到.

含硫量的计算式为:

$$S\% = T \times V / G \times 100\%$$

式中, T: NaOH 的滴定度, V: NaOH 的体积数, G: 称取煤或灰的重量.

由表 1 可知, 固硫率随着升温时间的延长而提高, 但有一个限度, 30min以后, 固硫率基

表 1 固硫率和升温时间的关系(从室温升到 450℃)

升温时间 /min	煤中硫含量 /%	平均值 /%	灰中硫含量 /%	平均值 /%	煤总量 /g	灰总量 /g	固硫率 /%
19	1.71	1.71	1.96	1.965	1.9884	1.3784	78.3
	1.71		1.97				
24	1.62	1.58	2.18	2.11	1.8988	1.1593	81.3
	1.54		2.04				
27	1.54	1.525	1.81	1.86	1.9631	1.3491	83.8
	1.51		1.91				
33	1.09	1.12	1.69	1.66	1.8659	1.0702	85.01
	1.15		1.63				
40	1.11	1.08	1.33	1.34	2.0078	1.3883	85.5
	1.01		1.35				
48	1.35	1.33	1.87	1.84	1.9111	1.1763	85.25
	1.31		1.81				

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表 2 固硫率和恒温时间的关系(恒温 t= 450℃)

恒温时间 /min	煤中硫含量 /%	平均值 /%	灰中硫含量 /%	平均值 /%	煤总量 /g	灰总量 /g	固硫率 /%
19	1.63	1.655	2.11	2.06	1.8435	1.1246	75.8
	1.68		2.01				
24	1.51	1.55	2.21	2.18	1.9762	1.0384	73.8
	1.59		2.15				
27	1.11	1.10	1.59	1.56	1.9374	0.9983	73.1
	1.09		1.53				
33	1.73	1.745	2.50	2.54	2.1035	1.0538	73.0
	1.76		2.58				
40	1.28	1.305	1.89	1.88	1.8938	0.9537	72.7
	1.33		1.87				
48	1.41	1.43	2.09	2.18	1.9583	0.9321	72.5
	1.45		2.27				

本上不再变化.

由表 2 可知, 19min 和 48min 的恒温时间对固硫率的影响不大, 仅相差 3.3% , 可略去不计.

由于温度为 450℃, 固硫率已达 80% 左右, 因此, 固硫反应主要发生在低温阶段, 高温阶段发生的是煤中碳的燃烧反应.

2 混有 Fe_2O_3 的 $CaSO_3$ 的性质

$CaSO_4$ 的生成有 2 种途径, 其中之一是通过 $CaSO_3$. 本节主要研究 $CaSO_3$ 在不同配比的 Fe_2O_3 含量下和温度之间的关系.

以 1kg 干煤粉重为基准, 按重量百分比 0‰、2‰、4‰、6‰、8‰把 Fe_2O_3 加入到 $CaSO_3$ 试剂中, 充分混合至均匀, 称取一定量的混合物于瓷舟中, 放入管式电炉里分别在 600℃、700℃、800℃、900℃、1000℃下恒温 1h, 同时通入一定量的空气.

将实验数据绘成图 1. 图 1 表明, Fe_2O_3 含量和温度对 $CaSO_3$ 的性质影响呈单一趋势, Fe_2O_3 用量增多, $CaSO_3$ 转化为 $CaSO_4$ 的量越多. 说明 Fe_2O_3 对 $CaSO_3$ 的氧化有促进作用. 不加 Fe_2O_3, 温度为 600℃时, $CaSO_3$ 的氧化率达 92%, Fe_2O_3 含量为 6‰时, $CaSO_3$ 转化率达 100%, 说明 $CaSO_3$ 在高温时的氧化速度比其分解速度要快得多, 温度越高, 氧化速度越快.

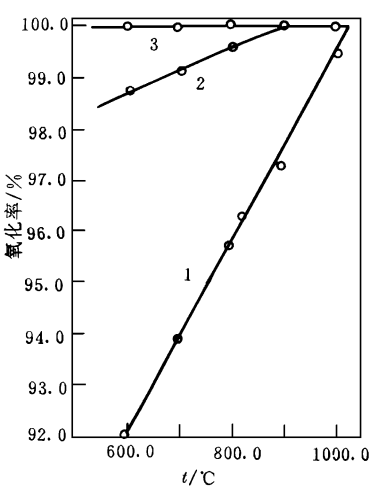

图 1 $CaSO_3$ 氧化率和温度的关系

1. Fe_2O_3 含量 0‰ 2. Fe_2O_3 含量 4‰ 3. Fe_2O_3 含量 6‰

3 Fe_2O_3 存在时 CaO 和 SO_2 的反应特性

在实际煤燃烧过程中, 无机硫或有机硫总是首先生成 SO_2, SO_2 转化为 SO_3 则通常是在催化剂的作用下, 否则速度较慢. 将 SO_2 和空气按一定比例混合通入电炉的石英玻璃管中, 管中瓷舟装有一定量的 CaO 和 Fe_2O_3 混合物,

分别在 300℃、400℃、430℃、450℃、470℃、500℃、600℃恒温 1h. CaO 的转化率和温度之间的关系为:

$$X\% = W_{FCaO}/W_{ZCaO} \times 100\%$$

式中, X: CaO 生成为 $CaSO_4$ 的转化率, W_{FCaO}: 反应转化为 $CaSO_4$ 的 CaO 质量(g), W_{ZCaO}: 用 EDTA 方法测得的CaO 质量(g).

将实验数据绘成图 2, 从图 2 可看到: Fe_2O_3 的含量相同, CaO 和 SO_2 反应生成 $CaSO_4$的转化率随温度升高而升高. 在相同的温度下, 加入 Fe_2O_3 比不加要优越得多, 说明 Fe_2O_3 的加入对硫的固 定确实起着较大的促进作用. 曲线 4 在 3 的下面, 说明并不是 Fe_2O_3 加得越多越好. 对固硫发生重大影响的仍是 CaO, Fe_2O_3 只是起着辅助作用.

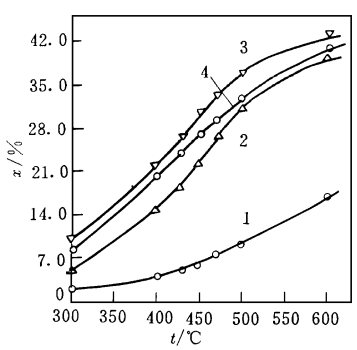

图 2　CaO 的转化率和温度的关系

1. Fe_2O_3 含量 0‰　2. Fe_2O_3 含量 4‰　3. Fe_2O_3 含量 6‰　4. Fe_2O_3 含量 8‰

4　固硫过程的主反应

对于反应 $CaO + SO_2 \rightarrow CaSO_3$, 由于 $CaSO_3$ 性质不稳定, 在空气中易氧化, 不便作全定量分析. 故在管式电炉中连续地通入 N_2 以置换其中空气, 在只有 N_2 存在的环境中可以认为 $CaO + SO_2$ 只生成 $CaSO_3$, 达到反应时间后, 切断 SO_2 和 N_2 气源, 立即通入空气, 且将反应温度升高到 700℃, 此时 $CaSO_3$ 全部转化为 $CaSO_4$, 分析 $CaSO_4$ 中 SO_4^{2-} 离子含量便可知 $CaO + SO_2$ 反应的快慢.

为研究反应 $CaO + SO_3 \rightarrow CaSO_4$, 在装有 $CaO + Fe_2O_3$ 的瓷舟前面放一段具有高催化性能的 V_2O_5, 目的是将 SO_2 部分地转化为 SO_3, 若 $CaO + SO_2 + 0.5O_2 \rightarrow CaO + SO_3 \rightarrow CaSO_4$ 是主反应, 则 $CaSO_4$ 生成量必将比由 $CaO + SO_2 \rightarrow CaSO_3 + 0.5O_2 \rightarrow CaSO_4$ 反应生成的量为多. 实验数据见表 3、4.

表 3　通 N_2 置换空气的对比实验

温度 /℃	Fe_2O_3 用量 /‰	CaO 反应量 /g	总 CaO 量 /g	转化率 /‰
400	0	0.06099	1.9842	3.07
400	6	0.1663	1.6478	10.09

表 4　通空气和 SO_2 且前段装 V_2O_5 的对比实验

温度 /℃	Fe_2O_3 用量 /‰	CaO 反应量 /g	总 CaO 量 /g	转化率 /%
400	0	0.06431	2.0133	3.19
400	6	0.1884	1.6001	11.77

由表3、4 可知: ①用 N_2 置换管式电炉中空气后, 可以认为炉中仅发生 $CaO + SO_2 \rightarrow CaSO_3$ 的反应, 加 Fe_2O_3 后 $CaSO_4$ 生成量增加了: 10.09% − 3.07% = 7.02%, 故可以认为 Fe_2O_3 是强化了 $CaO + SO_2 \rightarrow CaSO_3$ 的过程. ②通 N_2 时 $CaSO_4$ 生成率为 10.09%, 前段装入 V_2O_5, $CaSO_4$ 生成率为 11.77%, 两者相差甚微, 结合实际燃烧过程, 因 V_2O_5 催化性能远优于 Fe_2O_3, 可知由生成 SO_3 而加快生成 $CaSO_4$ 的反应并不明显.

综上所述, 下列两组反应中:

$CaO + SO_2 \rightarrow CaSO_3 + 0.5O_2 \rightarrow CaSO_4$

$CaO + SO_2 + 0.5O_2 \rightarrow CaO + SO_3 \rightarrow CaSO_4$

Fe_2O_3 主要是加快了 $CaO + SO_2 \rightarrow CaSO_3$ 这一过程. 而燃烧过程中硫是否生成 SO_3 则对固硫率影响不大.

参　考　文　献

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the lake; studies on the succession of phytoplankton; assessment of the fishery potential on the basis of phytoplanktonic primary productivity; determination of the standing crop and production of zooplankton; studies on the function of organic detritus in the system and the top-down effects of fish on the system, etc.

Key words: Lake Donghu, ecology, structure and functioning, top-down effects.

Thermal Environment of Urban Area and The Improvement of Its Micro-thermal Environment. Liu Xiaotu and Chen Enshui (Dept. of Architecture, Southeast University, Nanjing 210096), Shao Tieru (The Association for Science and Technology of Zhenjiang City 212001): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 54-58

On the basis of the change of thermal environmental factors in several cities and counties of southern part in Jiangsu province, this article analyzed firstly the changing trend of thermal environmental factors that caused by the urbanization, then introduced the effects for improving micro-thermal environment of habitation by using the measures including the planning of road network in urban area, the control of density of the buildings, the greenery and the waters in the urban area.

Key words: development of the cities, thermal environment, heat island effect, improvement of micro-thermal environment.

The Photolysis Character of Methyl Bromide and Tribromomethane in the Presence of Hydrogen Peroxide. Zhong Jinxian, Zhang Deqiang (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Chen Dazhou (Chinese Center for Certified Reference Materials, Beijing, 100013): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 59-61

Under simulated atmospheric condition, photolysis for $CH_3Br + H_2O_2$ and $CHBr_3 + H_2O_2$ systems were studied. H_2O_2 was irradiated by 253.7nm UV and produced OH radicals. The OH radicals can initiate photooxidation of $CHBr_3$ and CH_3Br. The products of photooxidation were determined by a fourier transform infrared spectroscopy with 20m long path cell. The products were CO, CO_2, CH_2O and H_2O for $CH_3Br + H_2O_2$ system, CO_2, CO, H_2O and $COBr_2$ for $CHBr_3 + H_2O_2$ system, based on those results the mechanisms of photooxidation were suggested.

Key words: photolysis, OH radicals, brominated methanes.

The Effect of Parents Smoking on the Urinary Concentration of 1-Hydroxypyrene of Children. Zhao Zhenhua (Beijing Municipal Research Academy of Environmental Protection, Beijing 100037), Tong Jingyi (Shanxi Provincial Children's Hospital, Taiyuan 030013): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 62-64

Using the urinary 1-hydroxypyrene as a biological index, the effect of parents smoking on the content of 1-hydroxypyrene in the pupil's urine was investigated. The 1-hydroxypyrene level in 234 urine specimens of pupils from 4 urban districts was determined, and the ambient air in these districts was synchronously sampled and analyzed for the content of benzo(a)pyrene (BaP). It was found that the content of urinary 1-hydroxypyrene of the pupils is significantly correlated with the ambient concentration of benzo(a)pyrene in the corresponding region where the school is located. For the groups of pupils whose parents smoke the urinary level of 1-hydroxypyrene are always higher than that of the groups with non-smoking parents, but the t-tests indicate that the difference is not statistically significant due to small populations.

Key words: smoking, urinary 1-hydroxypyrene, benzo(a)pyrene.

Primary Study on Sulfur Capture in Coal Briquet Combustion by Fe_2O_3 Promoting. Zhang Liangquan, Chen Siwei et al. (China Chemical Industry Economic and Technical Development Centre, Beijing 100723): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 65-67

According to the ignition point of sulphur in coal, the sulphur capture reaction process was divided into two stages in this paper. It was found that sulphur capture in coal ash mainly happened in stage of below 500℃. Relationship between time of raising temperature and fraction of sulphur capture was obtained that time of raising temperature must be below 30 min. It was found that the more Fe_2O_3 was used, the more $CaSO_3$ changed into $CaSO_4$. The actual process of sulphur captured in coal ash was simulated through the reaction $CaO + SO_2 + 0.5O_2 \rightarrow CaSO_4$. At last some special experiments were designed and proved that Fe_2O_3 mainly promoted the reaction $CaO + SO_2 \rightarrow CaSO_3$.

Key words: coal briquet, sulphur capture, Fe_2O_3.

Study on the Synthetizing Building Materials by Steam Curing Asbestos Tailings. Lu Zhongyuan, Wang Haibin et al. (Southwest Institute of Technolgy, Mianyang 621002): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 68-69

A Study on synthetizing the building materials by steam curing from asbestos tailing have been done in the present thesis. The effects of calcined temperature of the raw materials, the additions on the properties of products have been studied in this paper. The results showed that function of the material are the best when optimum temperature of pretreating the asbestos tailing is 950℃ and component in the material is 90% for the asbestos tailing and component in the material is all 5% for MA and NB.

Key words: asbestos tailings, building materials, steam curing.