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CaO 孔结构分形特性研究

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摘　要: 以分形理论为基础, 探讨了调质脱硫剂的孔结构特性。研究了添加剂含量及煅烧温度对 CaO 分形维数的影响。结果表明, 添加剂含量增多及煅烧温度升高, 均会造成 CaO 分形维数的下降。如在 900 ℃下, 当添加剂含量从 0.7% 增加到 3.4% 时, 分形维数约下降了 0.24。而在 2% 添加剂含量条件下, 当煅烧温度从 800 ℃升高至 1 000 ℃时, 分形维数约下降了 0.08。还研究了分形维数对 CaO 孔径分布的反映效果。分形维数下降, CaO 的孔径分布向大孔径方向偏移, 同时具有更大的最可几孔径, 表明分形维数可非常好的用于描述 CaO 孔径分布特性。

关　键　词: 调质脱硫剂; CaO; 煅烧; 孔径分布; 分形维数

中图分类号: X701.3　　文献标识码: A

引　言

常规钙基脱硫剂通过添加某些添加剂, 可以较大程度的促进脱硫剂的脱硫效果, 这已经被很多研究者所证实[1~10]。分析这些研究成果可发现, 钙基脱硫剂经添加剂处理前后, 其物理特性发生了很大程度的改变, 如孔结构。而脱硫剂的孔结构又是影响其硫化效果的重要因素之一, 因此, 对其孔结构的研究, 也一直是人们关注的重点。但综合已有的该方面的研究成果, 对调质脱硫剂的孔结构研究, 普遍还只是采用比表面积、孔隙率等常规参数进行描述。

分形理论是在 20 世纪 70 年代由 Mandelbort 创立的[11]。它是从几何学的角度, 研究欧氏空间中一类不可积的复杂系统。该类系统在结构、形状等方面具有自相似性。在欧氏空间, 维数通常是整数, 即几何结构是光滑和规则的。而对于分形结构来说, 维数通常是分数, 即几何结构是不光滑和不规则的。Mandelbort 进一步的研究发现, 欧氏测定不能抓住不规则形状的本质, 从而转向尺度对称性和尺度变换下的不变量—维数的研究。分形维数作为分形几何结构的一个重要参数, 反映了这种几何不规则的程度。

由于分形理论能更为真实、客观、细致地反映事物的内在本质, 目前已在包括多孔介质在内的许多研究领域中得到广泛的应用。近年来, 分形理论被逐渐应用到脱硫剂特性的研究中。在本文的工作中, 对几种工况下调质石灰石煅烧后产物 CaO 的分形维数进行了测定, 据此, 可对 CaO 的孔结构特性有进一步的理解。

1　实验样品及仪器

1.1　实验用石灰石的化学组成及制备

表 1　石灰石化学成分　　(%)

SiO_2	Fe_2O_3	Al_2O_3	$MgCO_3$	$CaCO_3$
0.12	0.24	0.09	3.17	96.38

石灰石平均粒径 31.4 μm。调质石灰石的制备方法为: 将石灰石浸泡于特定 Na_2CO_3/石灰石质量配比的 Na_2CO_3 溶液中 48 h, 然后置于干燥箱中 80 ℃下恒温干燥, 直至水分完全蒸发, 即可得需要样品, 期间没有添加剂的损失。

1.2　仪器及方法

采用 BJ－2 型差热天平进行石灰石的煅烧实验。实验时, 将热天平温度升到指定温度时再将样品放入其中。煅烧气氛为 8%O_2, 8%CO_2, N_2 作为平衡气氛。脱硫剂孔结构利用压汞仪测定。为以后叙述方便, 用 M-CaO 表示调质石灰石煅烧后产物, N—CaO 表示基质石灰石煅烧后产物。

2　实验结果及分析

2.1　配比对 M-CaO 分形维数的影响

已进行的研究表明[9~10], 调质石灰石中钠盐含

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量的多少，对其煅烧后产物 M-CaO 孔结构特性有重大的影响。因此，这里首先对几种配比调质石灰石，于 900 ℃下煅烧所得产物 M-CaO 的分形维数进行了测定，结果如图 1 所示。

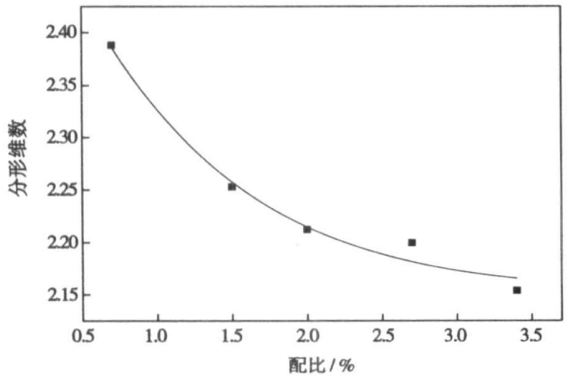

图 1 不同配比下煅烧所得 M-CaO 分形维数

图 1 表明，配比增加，M-CaO 分形维数逐步下降。分形维数是反映多孔介质孔结构不规则程度的物理量。其值越大，表明孔结构的不规则程度越大。由此可知，对于钠盐调质石灰石，随着向其中添加钠盐量的增多，煅烧产物 M-CaO 的孔结构越趋于规则。缪明烽指出，石灰石在分解过程中的烧结作用越大，孔结构的分形维数越小[12]。因而，分形维数可以反映出 M-CaO 的烧结程度。图 1 中的 M-CaO 分形维数随配比增加逐步下降的情形，表明添加剂量越多，M-CaO 的烧结越严重。前面对这几种 M-CaO 比表面积和孔隙率测量的结果，也证明了该结论的正确性[9~10]。

2.2 温度对 M-CaO 分形维数的影响

实验结果表明，不同温度下煅烧所得 M-CaO 具有不同的孔结构[9]。因此，这些 M-CaO 也就可能具有不同的分形维数。为了探讨煅烧温度对 M-CaO 分形维数的影响，选取了 2%配比调质石灰石，于不同温度下煅烧后得到 M-CaO，对其分形维数进行了测定，结果如图 2 所示。

图 2 表明，在所实验的温度范围内，M-CaO 分形维数随温度升高一直呈下降趋势。调质石灰石的煅烧温度升高，其分解速率会加快，完全分解时间会变短[9]。因而，从烧结时间角度讲，这会在一定程度上减轻烧结对产物 M-CaO 孔结构带来的不利影响。但对于钠盐调质石灰石，钠盐可能是决定产物 M-CaO 烧结特性从而影响到其孔结构的最主要因素。温度升高，钠盐对 M-CaO 烧结的影响程度加剧。特别是当煅烧温度超过钠盐的熔点(850 ℃)后，其加速 M-CaO 烧结的效应愈发明显。因而，尽管随煅烧温度升高，同时存在两个对烧结影响作用相反的过程，但由于钠盐对 M-CaO 烧结的促进作用占主导地位，因此出现图 2 中所示的随温度升高，M-CaO 分形维数逐步减小的情形。

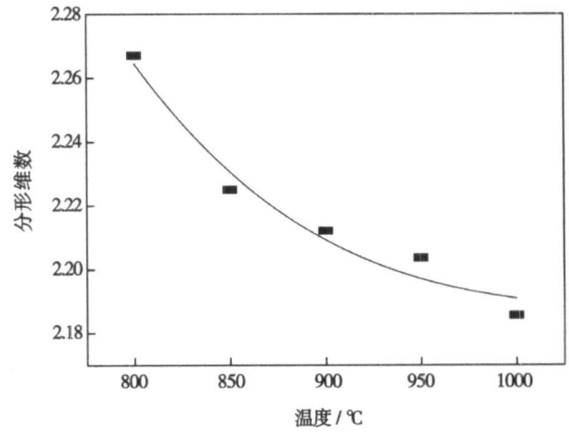

图 2 不同温度煅烧所得 2%M-CaO 分形维数

2.3 分形维数对 CaO 孔径分布的反映

有研究表明，分形维数可以反映出固体中孔隙分布的特性[12]。当多孔介质中的细微孔越多，孔结构的分形维数越大。因为细微孔越多，越容易造成孔表面不平整和不规则。为了获得对 M-CaO 孔分布特性与其分形维数关系的理解，利用 SEM 以及压汞仪的孔径分布曲线，进一步探讨了这种关系。

图 3 950 ℃下煅烧所得 N—CaO 颗粒表观形貌(×5000)

同样工况下，900 ℃下基质石灰石煅烧所得产物 N-CaO 的分形维数为 2.57。分析图 1 可知，同工况下煅烧所得 M-CaO 分形维数要小于 N-CaO 的分形维数。由此推测，M-CaO 的孔径分布比 N-CaO 向大孔方

向偏移。为了验证该推论, 选取 950 ℃下煅烧得到的 2%M-CaO 和 N-CaO, 进行了颗粒表观形貌 SEM 分析。扫描照片如图 3 ~图 4 所示。

图 4　950 ℃下煅烧所得 M-CaO 颗粒表观形貌(× 5000)

由这两幅扫描照片可非常清楚地看出, 同工况下煅烧所得 M-CaO 比 N-CaO 孔径明显加大。这表明利用分形维数来描述 M-CaO 孔径分布是适当的。

SEM 扫描照片毕竟只能提供定性的比较分析。为了对 CaO 分形维数与孔径分布的关系有进一步的理解, 需要进行量化的研究。如前所述, 900 ℃下煅烧得到的几种配比 CaO 分形维数的测定结果表明, 配比增加, 分形维数逐渐下降。由此可推测, 随配比增加, M-CaO 的孔径分布应逐渐向大孔方向偏移。为了验证该推测, 对这几种 CaO 孔径分布进行了测定, 如图 5(a) ~ (d)所示。

比较图 5(a) ~ (d), 可非常明显地发现, 随配比增加, M-CaO 的孔径分布向大孔径方向偏移, 同时具有更大的最可几孔径。通过上述 SEM 定性分析以及压汞仪定量描述, 表明分形维数可作为非常重要的一个工具, 用于表征 M-CaO 的孔分布特性。

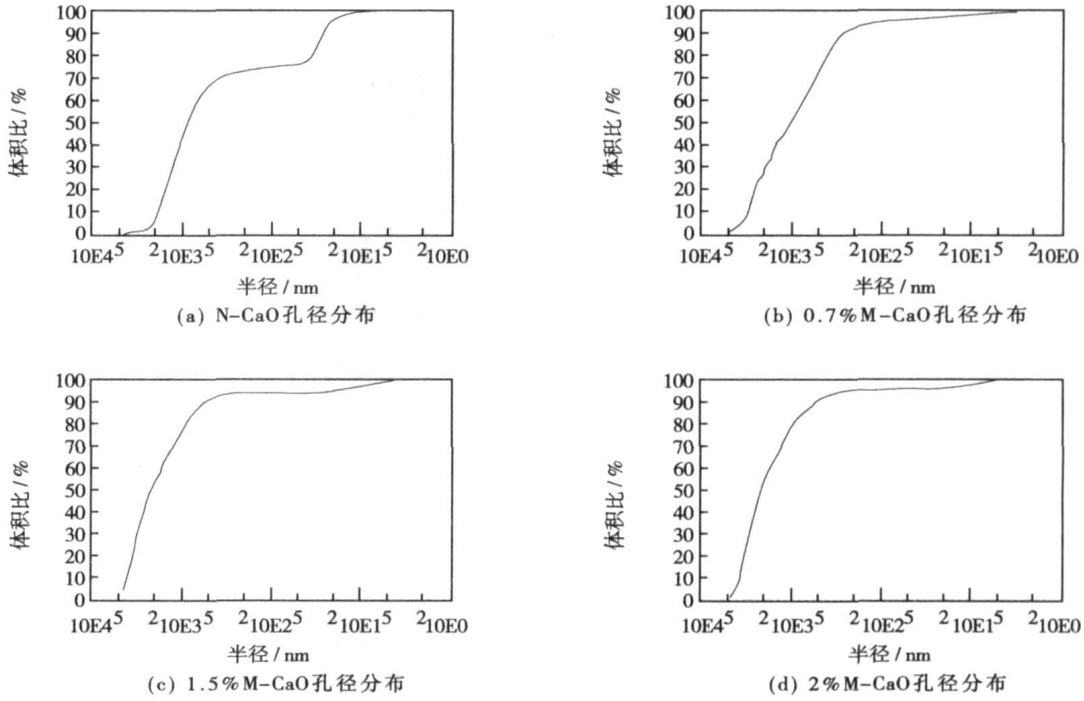

图 5　CaO 孔径分布

3　结　论

(1) 在所实验范围内, 添加剂含量增加, CaO 分形维数逐步下降。在 900 ℃下, 当添加剂含量从 0.7%增加到 3.4%时, 分形维数约下降了 0.24。这表明添加剂量越多, CaO 的烧结越严重。

(2) 在所实验的温度范围内, M-CaO 分形维数随温度升高一直呈下降趋势。而在 2%添加剂含量条件下, 当煅烧温度从 800 ℃升高至 1 000 ℃时, 分形维数约下降了 0.08。

(3) 通过 SEM 定性分析以及压汞仪定量描述,

表明分形维数可作为一个有效的工具，用于表征 CaO 的孔分布特性。分形维数下降，CaO 的孔径分布向大孔径方向偏移，同时具有更大的最可几孔径。

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（编辑 韩 锋）

新技术、新产品

陆用燃气轮机的紧凑型板式换热器

《Тяжелое машиностроение》2006 年 1～2 月号报道，ЦИАМ（俄罗斯中央航空发动机制造研究所）的专家们研究了用于陆用燃气轮机装置热量回收系统的紧凑型板式换热器。

计算研究结果的分析表明，为了从回热循环陆用燃气轮机装置得到最大的效率，换热器应该满足下列主要要求：

·热效率不低于 85%～90%；

·总的相对压力损失不大于 8%；

·在 2 000～5 000 次启动/停机循环下的寿命不小于 60 000～100 000 h；

·在批量生产情况下换热器的相对单价不大于 40～60 美元/kW。

提出了热量回收系统燃气—空气换热器设计的方法，考虑了关于质量尺寸、强度和运行指标的要求，包括用于回热循环陆用燃气轮机装置的高效板式换热器最佳模块的选择。

（吉桂明 供稿）

in various control processes. By the combined use of a prediction control and PID controller in the control of a reheat steam temperature system and with a neural network serving as a system prediction model, an on-line optimization has been performed of PID parameters through a chaos-based optimization algorithm. A computer-based simulation test has verified the effectiveness of the algorithm. Compared with the traditional PID control, the PID prediction control based on chaotic theory is capable of timely tracking system changes and overcoming any outside perturbations. As a result, achieved is a good control effectiveness and the exhibition of a very strong robustness performance. **Key words**: prediction control, PID (proportional-integral-differential) controller, chaos-based optimization, neural network, reheat steam temperature

凝汽器水下在线清洗机器人水动力特性研究＝**A Study of Hydrodynamic Characteristics of an Underwater On-line Condenser-cleaning Robot**[刊, 汉] / CHEN Ning, WAN Yi, PENG Wei, et al (Power Department, China University of Mining and Technology, Xuzhou, China, Post Code: 221009) // Journal of Engineering for Thermal Energy & Power. — 2008, 23(2). —183 ~ 186

By using a numerical simulation and related tests, a study has been performed of the hydrodynamic characteristics of an on-line-cleaning industrial robot destined for the condenser of a 300 MW steam turbine, which is now still under development. It is noted that the robot under discussion will not affect the normal operation of the condenser after being put into the return water chamber of the condenser, but there exist three unfavorable working zones for the operation of the robot. The first zone is located in a region above the condenser partition grate within a height five times of the tube diameter of the partition grate. The second unfavorable zone is situated at the robot's second-stage arm level in a region where the third-stage and second-stage arm form an included angle of 3 to 7 degrees. The third unfavorable zone is in a working region where the manipulator of the robot is pointing to the corner of the condenser. When the robot is working in the above-said unfavorable zones, the vibration of the robot manipulator will increase considerably, thus affecting the fixed location operation. Finally, the authors have conducted an exploratory study of the methods for coping with the above unfavorable zones and noted that an additional installation of a self-adaptive rotary flow-straightening hood on the arm rod of the robot is one of the effective measures. **Key words**: underwater robot, high pressure water jet flow, numerical simulation, vibration

CaO 孔结构分形特性研究＝**A Study of Fractal Characteristics of a CaO Porous Structure**[刊, 汉] / WANG Chun-bo, CHEN Chuan-min, LI Yong-hua, et al (Energy Source and Power Engineering Institute, North China Electric Power University, Baoding, China, Post Code: 071003) // Journal of Engineering for Thermal Energy &Power. — 2008, 23(2). —187 ~ 190

On the basis of fractal theory, an exploratory study has been conducted of the characteristics concerning the porous structure of a modified desulfuration agent. Furthermore, the influence of additive content and calcination temperature on CaO fractal dimension has also been studied. The research results show that the increase of both the additive content and calcination temperature can result in a decrease of CaO fractal dimension. For instance, at a temperature below 900 ℃, when the additive content increases from 0.7% to 3.4%, the fractal dimension will decrease by about 0.24. With the additive content being 2%, however, when the calcination temperature has increased from 870 ℃ to 1 000 ℃, the fractal dimension will decrease by about 0.08. In the meantime, the authors have also studied the effectiveness of reflecting the CaO pore diameter distribution by using the fractal dimension. With a decrease of the fractal dimension, the CaO pore diameter distribution will tend to shift to the direction of a bigger average pore diameter, and at the same time have a even bigger pore diameter, indicating that the fractal dimension can reflect exceedingly well the characteristics of CaO pore diameter

distribution **Key words**: modified desulfuration agent, CaO, calcination, pore diameter distribution, fractal dimension

氨法脱除燃煤烟气中 CO_2 的实验研究＝**Experimental Study of the Removal of CO_2 from Coal-fired Flue Gas by Using Ammonia**[刊, 汉] / ZHANG Mao, SAI Jun-cong, WU Shao-hua (College of Energy Science and Engineering, Harbin Institute of Technology, Harbin, China, Post Code: 150001), LI Zhen-zhong (National Research Center of Power Plant Combustion Engineering Technology, Shenyang, China, Post Code: 110034)// Journal of Engineering for Thermal Energy & Power. — 2008, 23(2). — 191 ~ 194

The removal of CO_2 greenhouse gas from coal-fired flue gas by spraying ammonia water is a new kind of CO_2 trapping method. To study the influence of such parameters as ammonia water concentration, CO_2 concentration and temperature on the CO_2 removal rate, an experimental study of ammonia water spray has been performed by employing a continuous on-line CO_2 detection in a stepped-ring packed tower operating at different parameters with diluted ammonia water serving as an absorption agent. The study results show that the diluted ammonia water also enjoys a relatively high rate of CO_2 removal. With an increase of the ammonia water concentration, the time required by the reaction to attain an equilibrium state and the CO_2 removal rate achieved at an equilibrium state will also gradually increase. With an increase of the initial CO_2 concentration in the flue gas, the CO_2 removal rate will decrease accordingly. In a temperature range from 22 to 50 ℃, the CO_2 removal rate is affected remarkably by the reaction temperature accompanied by a relatively conspicuous fluctuation of the rate in question. The removal rate will attain its maximum value at a temperature around 40 ℃. **Key words**: CO_2 greenhouse gas, ammonia water spray, packed tower, ammonium bicarbonate

甲烷/空气在微小型 Swiss-roll 燃烧器内燃烧的实验研究＝**Experimental Study of Methane/air Combustion in a Swiss-roll Miniature Combustor**[刊, 汉] / LI Jun-wei, ZHONG Bei-jing, WANG Jian-hua (Aeronautics and Astronautics College, Tsinghua University, Beijing, China, Post Code: 100084) // Journal of Engineering for Thermal Energy & Power. — 2008, 23(2). — 195 ~ 200

To understand the operation features of a miniature Swiss-roll combustor, a methane/air premixed combustion experiment has been performed with the combustion limit of the combustor being obtained. The influence of a heat recirculation on the combustion limit of the combustor has also been studied. The test results show that when the methane flow rate is between 0.8 and 2.7 mg/s, the miniature combustor thus designed can fulfill a stable methane/air combustion and guarantee that the flame is located at the combustor center. With the heat recirculation being enforced, the oxygen enrichment limit of the combustor will be decreased from 0.7 (without heat recirculation) to 0.5. However, the combustion limit is not symmetrical to ER (stoichiometric equivalence ratio) = 1. The fuel enrichment limit is small while the oxygen enrichment limit is large. At the same time, the authors have also conducted a numerical simulation of the miniature combustor. The simulation results show that the flow return zone at the combustor center enables the combustor to secure a stable operation in a relatively large range of combustion limit. **Key words**: miniature combustor, pre-mixed combustion, methane, combustion characteristics

高浓度水煤浆流变特性和稳定性试验研究＝**Experimental Study of High-concentration Coal-water-slurry Rheological Properties and Stability**[刊, 汉] / ZHAO Guo-hua, DUAN Yu-feng, XU Feng, et al (Education Ministry Key Laboratory on Clean Coal Power Generation and Combustion Technology, Southeast University, Nanjing, China, Post Code: 210096)// Journal of Engineering for Thermal Energy & Power. — 2008, 23(2). — 201 ~ 205