石灰石和白云石脱硫反应的加压热重分析研究*

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摘要　通过加压热重分析实验研究了石灰石及白云石在加压条件下的脱硫反应. 结果表明，在 0.85 MPa 和 900℃条件下，4 种石灰石及 2 种白云石的脱硫反应转化率均随时间延长而提高，120 min 时反应率在 23.5%—42%之间；在 1.15 MPa 和 750—950℃范围内，120 min 反应转化率均随温度提高而大幅度提高；在 860℃下，120 min 反应转化率随压力提高有小幅度线性增长. 最后探讨了脱硫反应机理.

关键词　加压热重分析，石灰石，白云石，脱硫反应.

随着煤炭利用技术的发展，包含一个加压燃烧环节的联合循环(如 PFBC-CC)已被公认为是极有前途的煤炭高效低污染利用方式，但是最常用的脱硫剂石灰石或白云石在这种条件下的脱硫反应报道尚不多见，在国外只有 Yrias P. 等[1]和 Buroni M. 等[2]进行过一些实验研究. 本实验用加压热重分析法(Pressurized thermogravimetric analysis，PTGA)研究了石灰石和白云石的脱硫反应，并探讨了石灰石和白云石脱硫反应机理.

1　实验部分

1.1　实验材料

实验所用 4 种石灰石和 2 种白云石平均颗粒直径均为 0.25 mm，其化学组成见表 1.

1.2　实验装置和方法

表 1　石灰石和白云石的化学组成/%(Wt)

矿　种	品　种	$CaCO_3$	MgO	Fe_2O_3	Al_2O_3	K_2O	S
石灰石	Boli	86.50	2.12	0.87	1.03	0.06	0.08
	Xuzhou	90.40	2.88	1.25	0.51	0.05	0.05
	Jiawang	93.40	3.06	1.53	0.48	0.11	0.04
	Songzi	87.10	1.55	0.62	1.24	0.08	0.05
白云石	Jinzhai	54.60	18.2	0.22	0.55	0.06	0.04
	Bengbu	50.70	16.9	0.18	1.68	0.05	0.06

加压热重分析实验装置为本单位自行研制，包括压力壳、反应器、样品架、微重量传感器、压力控制阀、温控器、流量显示及控制器和数据处理等部分. 试样量为 250 mg. 石灰石或白云石试样放在反应器中的铂金网状样品架内，反应气体自底部进入反应器，气体流量及脱硫反应压力由流量控制器和压力控制阀来调控. 反应温度可程序控制.

实验时，首先通入不含 SO_2 的混合气体(CO_2 和 O_2 浓度与含 SO_2 的反应气体相同)将反应器内压力升至实验压力，然后开始加热升温，待温度达到脱硫反应所需温度后，将气体切换成反应气体，开始脱硫实验，同时记录整个实验过程的 TG(热重)曲线.

1.3　实验压力和温度范围

采用典型的加压燃烧工况，实验温度范围

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为750—950℃，反应气体中CO_2浓度为20%. 此时只要保证反应气体总压力达到0.50—1.15 MPa，就可使CO_2分压大于$CaCO_3$分解压力[2]，这样就可满足脱硫反应要求.

2 结果和讨论

2.1 转化率随时间的变化和石灰石及白云石品种对脱硫反应的影响

图1是4种石灰石和2种白云石脱硫反应转化率随时间的变化关系.

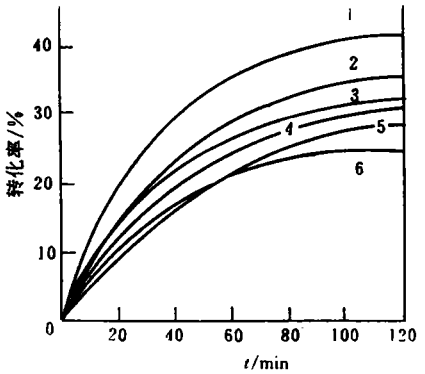

图1 石灰石和白云石脱硫反应转化率随时间的变化

石灰石：1. Boli 2. Xuzhou 4. Songzi 5. Jiawang

白云石：3. Jinzhai 6. Bengbu

压力：0.85 MPa 反应温度900℃

浓度：SO_2 0.342% CO_2 20% O_2 5% N_2 75%.

图1表明，石灰石和白云石在加压条件下可以有效地与SO_2直接进行反应，其转化率并不比常压条件下低[3]. 这说明加压条件下石灰石或白云石仍然是有效的脱硫剂.

图1还表明，白云石和石灰石品种对反应有明显影响. 总体说来，石灰石的脱硫反应转化率高于白云石，但不同来源的各种矿石转化率差别很大，如Boli石灰石120 min转化率竟高出Jiawang石灰石14%. 不同来源的矿石，虽然其主要化学成分相近，但各自晶体结构不同所以反应活性不同. 另外，随着脱硫反应的进行，固体颗粒外层将为$CaSO_4$反应产物层包裹，反应气体必须扩散通过这个产物层才能达到反应表面，由于反应物晶体致密程度的不同，某些$CaSO_4$产物层较松疏，对进一步反应有利；反之亦然.

2.2 温度对脱硫反应的影响

图2是温度对反应影响的实验结果. 从图2可看出，在实验温度750—950℃范围内，各种石灰石和白云石脱硫反应转化率均随温度升高而大幅度增加. 这与常压条件下情况不同[3]. 常压条件下，石灰石脱硫反应的最佳温度为850—900℃，当超过这个范围后，转化率就下降.

同样，6种石灰石、白云石脱硫反应转化率随温度升高的变化幅度不同. 在750℃下和950℃下其转化率呈现不同的高低顺序.

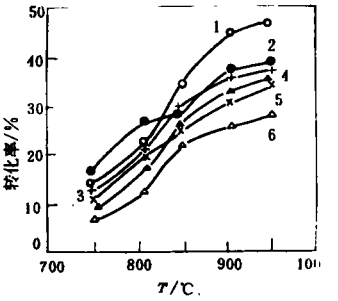

图2 温度对脱硫反应的影响

石灰石：1. Boli 2. Xuzhou 4. Songzi 5. Jiawang

白云石：3. Jinzhai 6. Bengbu

反应条件：压力1.15 MPa，反应温度120 min，

反应气体成分同图1

2.3 压力对脱硫反应的影响

反应气体压力对石灰石和白云石脱硫反应转化率的影响关系见图3. 由图3可见，随着压力增加，反应转化率有小幅度线性增长. 因为反应速度与系统压力的反应级数次方成正比，所以可以认为这是一个一级反应.

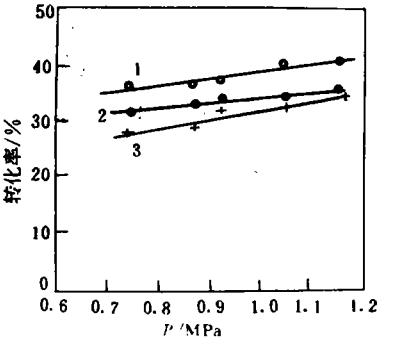

图3 压力对脱硫反应的影响

石灰石：1. Boli 2. Xuzhou 白云石：3. Jinzhai

反应条件：反应时间120 min，温度850℃，

反应气体成分同图1

2.4 脱硫反应机理分析

常压条件下石灰石或白云石中的 $CaCO_3$ 遇热首先分解为多孔状 CaO，继而与烟气中 SO_2 在富氧条件下形成 $CaSO_4$，在典型的加压燃烧工况下，CO_2 分压高于 $CaCO_3$ 平衡分解压力，故 $CaCO_3$ 不能分解，这时 $CaCO_3$ 将按下式与 SO_2 直接进行反应：

$$CaCO_3(S)+\frac{1}{2}O_2(g)+SO_2(g)\longrightarrow CaSO_4(s)+CO_2(g) \quad (1)$$

这是一个气-固非均相反应，包括下列 3 个过程：① 反应气体由气相主体向石灰石或白云石固体颗粒表面传质；② 反应气体通过 $CaSO_4$ 产物层向固体表面扩散；③ 气-固表面化学反应. 在反应初始阶段，$CaSO_4$ 层很薄，因此扩散阻力很小，脱硫反应受化学反应所控制. 根据石灰石脱硫反应初始阶段(本文选择 220 s)转化率随时间的变化关系实验数 据(如图 1)可以求出 K_s；再根据整个实验曲线求出 D_e，求出 φ.

$$\varphi=\sqrt{\frac{K_sR_p}{6D_e}} \quad (2)$$

式中，R_p 为固体颗粒半径，K_s 为气固表面化学反应速度常数；D_e 为有效扩散系数.

如果 $\varphi<0.1$，则认为系统受化学反应控制，如 $\varphi>10$，则认为系统受通过产物层扩散控制. 根据图 1 计算出的 K_s、D_e、φ 结果见表 2. 这说明石灰石和白云石在加压条件下的脱硫反应，除了反应初始阶段外，同时受化学反应和产物层扩散控制.

表 2　K_s 和 D_e 模型计算结果

矿　种	品　种	K_s/m·s^{-1}	D_e/m^2·s^{-1}	φ
石灰石	Boli	1.46×10^{-3}	4.47×10^{-9}	3.69
	Xuzhou	1.02×10^{-3}	3.50×10^{-9}	3.48
	Jiawang	9.25×10^{-4}	2.48×10^{-9}	3.94
	Songzi	1.28×10^{-3}	3.06×10^{-9}	4.17
白云石	Jinzhai	1.35×10^{-3}	2.97×10^{-9}	4.35
	Bengbu	7.72×10^{-4}	3.15×10^{-9}	3.20

根据不同反应温度的实验结果，由数学模型可计算出不同温度时的 K_s 和 D_e 值，再采用 Arrhenius 方程可以计算得到表面化学反应和产物层扩散控制的表观活化能 E_K 和 E_D(见表 3).

表 3　表观活化能 E_K 和 E_D 计算结果

矿　种	品　种	E_K/kJ·mol^{-1}	E_D/kJ·mol^{-1}
石灰石	Boli	64.3	109
	Xuzhou	75.2	149
	Jiawang	69.4	176
	Songzi	78.5	181
白云石	Jinzhai	70.9	135
	Bengbu	81.6	152

由表 3 可以看出，石灰石和白云石品种对其表面化学反应及产物层扩散控制过程的表观活化能均有显著的影响，从而影响转化率的顺序变化.

脱硫反应式(1)表明这是一个气体体积降低的反应. 根据化学平衡一般规律，提高系统压力，平均向右移动，有利于反应进行. 这就很好地解释了压力对转化率的影响.

3 结论

(1) 在 0.85 MPa，900℃条件下，4 种石灰石和 2 种白云石的脱硫反应转化率均随时间延长而提高，120 min 时转化率在 23.5%—42% 之间.

(2) 在 1.15 MPa，750—950℃范围内，120 min 的反应转化率均随温度提高而大幅度提高，但不同品种的矿石提高幅度不同.

(3) 在 860℃下 120 min 反应率随系统提高有小幅度线性增长.

(4) 石灰石和白云石在加压条件下的脱硫反应，除了初始阶段外，同时受化学反应和产物层扩散控制；温度改变，则使表观活化能 E_k 和 E_D 发生变化，进而影响转化率的顺序变化；反应前后气体体积降低，所以提高系统压力，有利于反应进行.

参 考 文 献

1　Yrias P, Lisa K. Hupa M. Fuel, 1995, **74**: 395

2　Buroni M, Carugati A, Piero G D et al. Fuel, 1992, **71**: 919

3　邱宽峰. 中国环境科学, 1994, **14**(2): 119

by Plasma. Liu Zhengchao et al. (Environ. Science Institute, Fudan University, Shanghai 200433), Pan Xuxi et al. (Dept. of Physics I, Fudan University, Shanghai 200433): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 21—23

In order to apply plasma technology in environmental protection, and find a new way to treat air pollutants, the experiment selected CF_2ClBr, a kind of chemical stable extinguisher as the research material, and the influence of He, N_2, O_2 and air in degradation of CF_2ClBr by plasma was studied, and CF_2ClBr was successfully degraded at normal pressure. The main products of degradation were similarly to only degrading CF_2ClBr when He or N_2 was added to the degradation system. The degradation products was mainly CF_2O, Br_2, Cl_2 in the presence of O_2 and air. The order of extra gases influencing degradation of CF_2ClBr was following: $He<N_2<O_2$, air.

Key words: CF_2ClBr, plasma, degradation.

Photodissociation of CF_2ClBr at 185 nm of Ultraviolet Radiation. Duan yang et al. (Institute of Environmental Science, Fudan University, Shanghai 200433), Zhu Shaolong et al. (Institute of Electric Light Sources, Fudan University, Shanghai 200433): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 24—26

The photodissociation of CF_2ClBr and its photooxidation at the existence of O_2 at 185 nm of ultraviolet radiation were studied using low pressure mercury lamp. The results showed that the dissociation of pure CF_2ClBr at 185 nm of ultraviolet radiation is a balance reaction, and the ultimate dissociation rate is about 26%. The dissociation of CF_2ClBr is a first order reaction and the rate constant is $1.70\times10^{-3}\ s^{-1}$ at the existence of O_2. The dissociation procedure of CF_2ClBr at 185 nm of ultraviolet radiation and the mechanism of its photoreaction with O_2 was discussed.

Key words: CF_2ClBr, photodissociation, photooxidation.

Computation of the A-Weighted Insertion Loss for Sound Barriers Used in Traffic Noise Control of Elevated Complex Road. Chen Ziming and Wang Shuquan (Dept. of Physics, Ocean University of Qingdao, Qingdao 266003): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 27—30

In order to solve the problem of computing the insertion loss of sound barriers used on elevated complex roads, this paper presented the computation method of the A-weighted insertion loss of sound barriers installed at different positions for different types of vehicles, different speeds, and different vehicle flows. It was found that the computational results are generally in agreement with measurements, the error is less than 1.5 dB(A). This model is of practical significance for the estimation of traffic noise of elevated complex roads with sound barriers, especially at night when traffic flow is relatively low.

Key words: traffic noise, elevated complex road, sound barrier, insertion loss computation.

Basic Study for the Formation of Trihalomethanes (THMs) in Chlorination Process of Humic Acid. Pan Jinfang and Zhang Danian (East China University of Science & Technology, Shanghai 200237), Maeda Yasuaki and Kitano Masaru (Osaka Prefecture University, Sakai, Osaka, Japan): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 31—33

In order to study carcinogenic by-products for example chloroform in disinfection of drinking water with chlorine, the research on reaction between low molecular weight humic acid and sodium hypochlorite which produced chloroform was carried out. The experimental results indicated that under certain temperature, certain concentration of sodium hypochlorite and pH, the amount of chloroform produced increased with the increase of the concentration of humic acid. When pH was in the range of 7.3—9.0, the chloroform-producing rate was the fastest. When pH was higher than 9.0, the chloroform-producing rate decrease with the increase of pH. The amount of chlorofom produced was in direct proportion to temperature. The activated energy that chlorinated humic acid to chloroform was 51.8 kJ. So the effective way to decrease the concentration of chloroform was to decrease the concentration of humic acid in the water.

Key words: humic acid, chlorination, chloroform.

A Study on Photocatalytic Reduction of Cr(Ⅵ) in Aqueous Solutions Using Ultrafine Powders of Oxide Semiconductors. Dai Xiaming, Chen Yonghua et al (Beijing Fine Ceramic Laboratory, Tsinghua University, 102201, Beijing): *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 34—36

The photocatalytic reductions of Cr(Ⅵ) in aqueous suspensions of ZnO/TiO_2 under UV illumination were investigated. The study had been performed by determination of the amount of Cr(Ⅵ) photoreduced at different kinds of irradiations, different reaction times, pH and organic additives. The results obtained showed that the concentration of Cr(Ⅵ) decreases apparently by the new kind of treatment. The efficiency of ZnO is higher than TiO_2 in same reaction condition. The concentration of Cr(Ⅵ) is reduced from 100 mg/L to below 0.47 mg/L after 90 min treatment by using ZnO powder as catalyst at optimum condition. It was found that the presence of organic additive and the lower pH can increase the reduction ratio of Cr(Ⅵ). The reaction mechanism and the relation between reaction rate and Cr(Ⅵ) concentration were also discussed. The technique is convenient for existing industrial processing of reduction of Cr(Ⅵ).

Key words: photocatalytic reduction, Cr(Ⅵ), ZnO/TiO_2.

Pressurized Thermogravimetric Study on the Reaction of Desulfurization by Limestones and Dolomites. Qiu Kuanrong et al. (Dept. of Coal Utilization, China, Univ. of Min. & Tech., Xuzhou 221008): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 37—39

The desulfurization reaction of limestones and dolomites was studied by pressurized thermogravimetric analysis method. Results showed that the rate of converting $CaCO_3$ to $CaSO_4$ of four limestones and two dolomites is in-

creasing with reaction time under conditions of 0.85 MPa and 900℃, and the conversion rate is in range of 23.5% to 42% at 120 minutes. The conversion rate is drastically growing with temperature under conditions of 1.15 MPa and 750—950℃ at 120 minutes. The conversion rate was slowly and linearly increasing with pressure under condition of 860℃. Finally, the reaction mechanism was discussed.

Key words: pressurized thermogravimetric analysis, limestone, dolomite, desulfurization.

Study on the Regeneration of $NaHSO_3$ in the Recovery of SO_2 from Flue Gas by Bipolar Membrane Electrodialysis. Yu Lixin et al. (Department of Chemical Engineering, Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 40—42

Bipolar membrane electrodialysis is adopted in the regeneration of $NaHSO_3$, which is used as absorbent of SO_2 from flue gas. When cation-exchange membrane is supplemented with , both homogeneous and heterogeneous bipolar membranes which are made in our lab and by Shanghai Chemical Factory, respectively, can produce satisfactory conversion ratio (higher than 80%) in the regeneration process. The decrease of current efficiency (from approximately 80% to approximately 20%) is resulted from the increase of the concentration of proton in acid chamber. The existence of small amount of Na_2SO_4 in $NaHSO_3$ solution doesn't cause much effect on regeneration process. The short membrane lifetime hinders the process from getting into practical application.

Key words: bipolar membrane electrodialysis, recovery of SO_2 from flue gas, regeneration of $NaHSO_3$.

Study on Characterization of Adsorption of Zine onto five types of soil in Beijing Area. Zhou Wei and Li Jiyun (Research Center for Eco-Enviromental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 43—45

The results of study on adsorption of zine onto five types of soil in Beijing area showed that the capacity of five types of soil adsorbing zine presents positive correlation with pH volue of the soil solution, contents of organism and $CaCO_3$ etc in soil. The adsorption data could be fitted to the Freundlich-type equation.

Key words: adsorption, zine, soil, Beijing area.

A Study on Acclimation Technique of Activated sludge and Biological Treatment of High Consistence Cheni-thermomechanical Pulp Wastewater. Chen Min (Guangdong University of Technology, Environment & Resource Engineering Department, Guangzhou, 510090), Sung-Nien Lo and H-Claude Lavallée (Université du Québec à Trois-Rivières, Québec, Canada, G9A 5H7): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 46—49

The treatment of high consistence Cheni-thermomechanical Pulp (CTMP) pulping wasterwater using activated sludge method was studied in this paper. The effect of improving technique in activated sludge acclimation on the sludge settleability and removal efficiencies was discussed. The Experiments showed that the improved technique i. e combination of batch and continous feed in sludge acclimation process can remarkably improve the sludge settleability and removal efficiencies. The sludge volume after 30 minutes of settling was 290—320 ml/L, sludge volume index was 48—55 ml/g, the removal of COD reached to 77%—85%, removal of BOD_5 was 90%—95%, removal of TSS was 75%—89%.

Key words: batch feed, continous feed, activated sludge, acclimation technique, CTMP wastewater.

Test of Tar Emulsified Liquid as Dust Suppressant for Dirt Roads. Wu Chao et al. (Dept. of Resources Exploitation Engineering, Central South University of Technology, Changsha 410083): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 50—52

In order to control the dust raising on the dirt roads efficiently, the tar emulsified liquid with low concentration was taken as the dust suppressant. Based on a great number of experiments in laboratory, the optimum compositions of surfactants and the prepared condition for emulsifying tar were achieved, tar is 3%—6%, surfactants is 0.5% and water is 93.5%—96.5 Wt. %. The prepared temperature is greater than 70℃. Depended on a lot of tests both in laboratory and field, the results showed that the liquid is very efficient for binding dust and maintaining the dirt roads. The active time can reach more than 10 days, when the liquid is sprinkled on the road in 2.2 kg/m^2. A rational profit can also be achieved after it is used for years.

Key words: dust suppressant for roadway, tar emulsified liquid, field test.

Electrochemical Separation Process for Recovery of Gold, Silver and Lead from Scrap. Liang Huqi et al. (Dept. of Chem. Eng., Shanghai University, 200072): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 53—56

The electrochemical separation process for comprehensive recovery of gold, silver and lead from Au, Ag-containing scrap was investigated. The smooth and dense cathodic deposit with purity of 99% Pb was prepared by electrochemical separation process under the optimum technological conditions (electrolyte composition: 70 g/L Pb^{2+}, 100 g/L total SiF_6^{2-}; solution temperature: 40 C. current density: 100 A/m^2; concentration of β-naphthol tobone glue: 0.002 g/L and 0.5 g/L) experimentlly. The current efficiency of lead was higher than 98%, the specific electric energy consumption was 117 kW · h/tPb. The recovery of Au and Ag in the anode slime were as high as 99% and 98% respectively.

Key words: recovery of Au and Ag, electroche mical separation, treatment of scrap.

Effects of Low pH Value and Aluminum on Uptake of ^{45}Ca by *Misgurnus anguillicaudatus*. Kong Fanxiang et al. (Dept. of Environ. Sci. and Eng., Nanjing University, Nanjing 210093): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 57—59

The effects of low pH value and with or without the addition of aluminum on the uptake of ^{45}Ca by *Misgurnus anguillicaudatus* were studied. The results showed that