

外加气体对等离子体降解 CF_2ClBr 的影响*

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摘要 用等离子体处理难降解大气污染物是近年国内外研究较活跃的领域, 选用化学方法难降解的 CF_2ClBr 为对象, 研究了 He 、 N_2 、 O_2 及空气对等离子体降解 CF_2ClBr 的影响, 实现了 CF_2ClBr 的常压解离。外加气体为 He 、 N_2 时 CF_2ClBr 的降解情况与纯 CF_2ClBr 的降解基本相同, 外加气体为 O_2 、空气时主要降解产物为 CF_2O 、 Br_2 、 Cl_2 。外加气体对降解的影响大小为 $\text{He} < \text{N}_2 < \text{O}_2$, 空气。

关键词 CF_2ClBr , 等离子体, 降解。

70 年代以来, 科学家认为南极臭氧空洞的形成与人类所排放 CFCs 及 Halon 类物质有关。Halon 类物质在大气中的寿命很长, 约为 100 年^[1], 完全能通过扩散进入平流层。本实验用高频电源产生电晕放电, 初步研究了 He 、 N_2 、 O_2 及空气对降解 CF_2ClBr 的影响。

1 实验部分

1.1 材料与仪器

(1) 气体原料 CF_2ClBr (99.5%), 上海制冷剂厂; He (99.99%), 北京氧气厂; N_2 (99.99%), O_2 (99.5%), 上海浦江特种气体供应站; 压缩空气, 上海比欧西气体工业有限公司。所有气体使用前未进一步纯化。

(2) 实验仪器 102G 气相色谱仪(上海分析仪器厂); HP8542A 型 UV-Vis 分析仪(美国惠普公司); Nicolet 5DX 型 FT-IR 红外仪(美国 Nicolet 公司); 真空系统、配气系统、进样系统各一套; 等离子体电源及自制玻璃等离子体样品管一支。

1.2 实验方法

实验方法见参考文献[2]

2 实验结果与讨论

2.1 纯 CF_2ClBr 的降解

CF_2ClBr 的压强为 $2.67 \times 10^3 \text{ Pa}$, 用高频电

源放电 2 min 后, 主要降解产物为: CF_3Cl , Br_2 , CF_4 , CF_2Cl_2 。 CF_2ClBr 的解离率为 90.5%, 增大 CF_2ClBr 的初始压强, 解离率随压强的增大急剧下降, 至 $5.4 \times 10^4 \text{ Pa}$ 时几乎不再解离^[2]。

2.2 外加气体对降解 CF_2ClBr 的影响

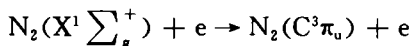
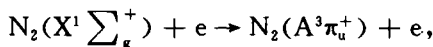
(1) He 对降解 CF_2ClBr 的影响 外加气体为 He , CF_2ClBr 的解离率随 He 分压的增大缓慢下降, 当 $P_{\text{He}} = 1.01325 \times 10^5 \text{ Pa}$ 时, CF_2ClBr 仍有 79.9% 的解离率(图 1), 主要降解产物为 CF_3Cl , Br_2 , CF_4 , CF_2Br_2 (1153 cm^{-1} , 831 cm^{-1})^[3](图 2a) 及少量 SiF_4 , CF_2Cl_2 , CF_2O , 从 FT-IR 谱来看与 CF_2ClBr 纯态时的解离情况基本相同^[2]。这个结果是必然的, 因为 He 是惰性气体, 其电离能为 24.578 eV, 在本实验条件下, 电子不足以使它电离, 故 He 不会参与 CF_2ClBr 的降解。 $P_{\text{He}} = 1.01325 \times 10^5 \text{ Pa}$ 时 CF_2ClBr 的解离率降到 79.9% 是因为 He 压强增大时, 它与电子之间的碰撞过于频繁使电子失去了部分能量, 从而使解离率降低, 这也证明了电子与 He 之间的碰撞不完全是弹性碰撞。

(2) N_2 对降解 CF_2ClBr 的影响 N_2 的键能为 9.82 eV, 与体系中能量高的电子差不多, 少量 N_2 在高速电子的碰撞下会分解为 N 或形成

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激发态的 N_2 , 如:



处于激发态的 N_2 能参与 CF_2ClBr 的降解, FT-IR 谱(图 2b)证实了这一点, 在 $1650-1970 \text{ cm}^{-1}$ 之间出现了许多小峰, 其中可能有 NOF , $NOCl$ 等的吸收峰, 其他产物与纯态时的降解产物基本相同^[2]. CF_2ClBr 的解离率也随 N_2 分压

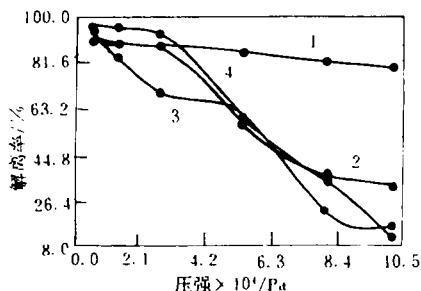


图 1 CF_2ClBr 的解离率与外加气体压强的关系

1. He 2. N_2 3. O_2 4. Air

$P_{CF_2ClBr} = 2.67 \times 10^3 \text{ Pa}$

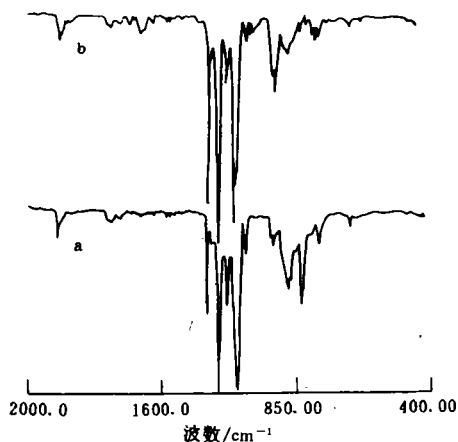


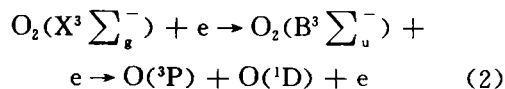
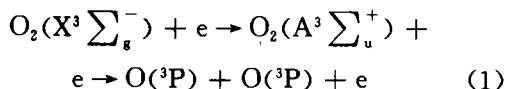
图 2 CF_2ClBr 与 He 和 N_2 经 2 min 放电后 FT-IR 谱

a. $2.67 \times 10^3 \text{ Pa } CF_2ClBr + 1.33 \times 10^4 \text{ Pa He}$ 降解后

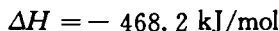
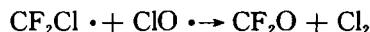
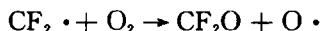
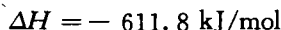
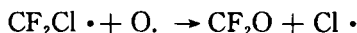
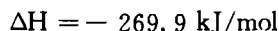
b. $2.67 \times 10^3 \text{ Pa } CF_2ClBr + 1.33 \times 10^4 \text{ Pa } N_2$ 降解后

的增大而降低(图 1), N_2 的分压为 $1.01325 \times 10^5 \text{ Pa}$ 时, CF_2ClBr 的解离率为 32.0%, 这从电子自由程的缩短和 N_2 的激发及分解要吸收部分能量是可以得到解释的. 同时也反映了电子与 N_2 之间的碰撞非弹性程度比 He 要高.

(3) O_2 对降解 CF_2ClBr 的影响 O_2 比 N_2 活泼, 其键能为 5.12 eV, 基态的 O_2 被能量较高的电子碰撞后会激发或分解:



其中(1)式所需的电子能量为 6 eV, (2)式所需的电子能量为 8.4 eV^[4], 处于激发态的 O_2 或 O 与 $CF_2Cl \cdot$, $CF_2 \cdot$ 等反应, 通过下列途径生成 CF_2O :



产物 CF_2O 比 CF_3Cl , CF_4 , CF_2Cl_2 稳定. 有 O_2 存在时, CF_2ClBr 的降解主要是通过以上反应进行, 从反应历程来看, 产物主要为 CF_2O , 还应有 Cl_2 或 ClO_x . FT-IR 谱(图 3b)及 UV-Vis 谱(图 4b)证实了这一点, 主要降解产物为: CF_2O (1941 cm^{-1} , 1249 cm^{-1} , 956 cm^{-1} , 775 cm^{-1})^[5], Br_2 ^[6, 7], Cl_2 ^[6, 8], SiF_4 及少量 CF_4 , $COClF$, ClO_x 等在 UV-Vis 光谱中未检测到. 有 O_2 存在的条件下另一个特点是: SiF_4 的生成量大, 这可能与气体中存在微量的 H_2O 有关, 通过反应: $CF_2O + H_2O \rightarrow CO_2 + HF$, $HF + SiO_2 \rightarrow SiF_4$ 生成 SiF_4 . 氧分压对降解产物也有影响, 氧分压低时生成较多的 CF_4 , 较高时主要为 CF_2O , 同时 CF_4 的生成量下降, 这说明生成 CF_2O 能使降解后的体系更稳定. CF_2ClBr 的解离率随 O_2 分压的增大下降较快(图 1), $P_{O_2} = 1.01325 \times 10^5 \text{ Pa}$ 时, 解离率为 15.0%, 比外加气体为 N_2 时要低, 这从 O_2 比 N_2 更容易从碰撞中获得能量得到充分的解释.

(4) 空气对降解 CF_2ClBr 的影响 从 FT-

IR 谱(图 3c)来看,空气中的 N_2 没有参与 CF_2ClBr 的降解,原因是 O_2 存在, CF_2ClBr 的降解主要是通过与 O_2 反应这个途径进行的,这说明了 O_2 比 N_2 更容易参与 CF_2ClBr 的降解,降解产物与外加 O_2 时几乎一样. 空气分压为 1.01325×10^5 Pa, 解离率仅为 11.5%, 这时产物也很单一,基本上只有 CF_2O .

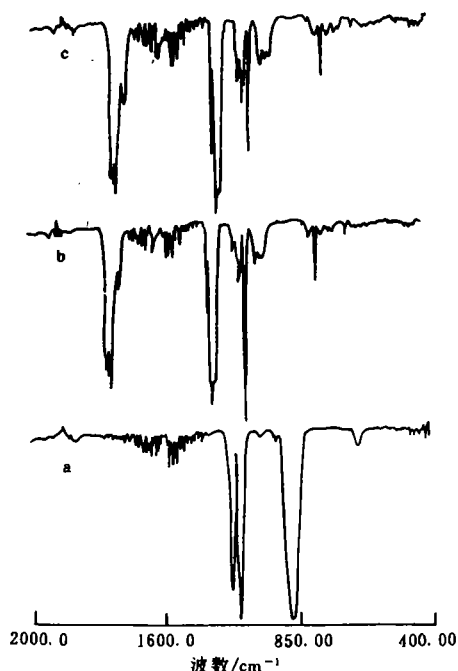


图 3 CF_2ClBr 与 O_2 和空气经 2 min 放电后的 FT-IR 谱

- a. 2.67×10^3 Pa CF_2ClBr + 1.33×10^4 Pa O_2 降解前
b. 2.67×10^3 Pa CF_2ClBr + 1.33×10^4 Pa O_2 降解后
c. 2.67×10^3 Pa CF_2ClBr + 1.33×10^4 Pa 空气降解后

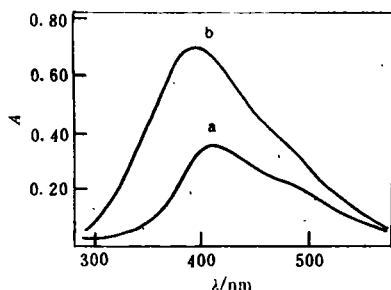


图 4 CF_2ClBr 经 2 min 放电后的 UV-Vis 谱

- a. 1.33×10^4 Pa CF_2ClBr
b. 1.33×10^4 Pa CF_2ClBr + 1.33×10^4 Pa O_2

2.3 含氧气体对降解 CF_2ClBr 的影响

CF_2ClBr 的压强为 2.67×10^3 Pa 及外加气

体压强为 1.33×10^4 Pa 时,外加含氧气体,主要降解产物为 CF_2O , Br_2 , Cl_2 , 与纯态及外加 He、 N_2 时的产物 CF_3Cl 、 Br_2 、 CF_4 、 CF_2Cl_2 区别很大. CF_2O 是加入了 O_2 直接引起的,但 Br_2 和 Cl_2 在产物中的含量尤其是 Cl_2 在量上的变化也与 O_2 有关, O_2 能参与 CF_2ClBr 的降解,降解产物 CF_2O 很稳定,氯在降解后以 Cl_2 存在,这表明降解后体系的能量比外加 He、 N_2 时进一步降低, Cl_2 和 Br_2 量的大小反映了降解后体系总能量的高低. 加入对降解影响最小的 He 时,溴除 Br_2 存在外,还以 CF_2Br_2 等形式存在(图 2a),氯主要存在于 CF_3Cl (图 2a); 加入 N_2 时含溴化合物的量减少(图 2b); 加入对降解影响大的 O_2 和空气,含溴化合物进一步减少(图 3 b, c),含氯化化合物的量也减少, Br_2 和 Cl_2 的量相应增加,尤其是 Cl_2 的量增加非常明显(图 4 b). 图 4a 为 1.33×10^4 Pa 纯 CF_2ClBr 降解后的 UV-Vis 谱,吸收峰与 Br_2 的峰形^[6]及峰位^[7]完全一致,可以断定降解后的产物中只有 Br_2 ; 图 4b 为 1.33×10^4 Pa CF_2ClBr 与 1.33×10^4 Pa O_2 降解后的 UV-Vis 谱,图中不但吸收峰位移到 386 nm 而且在 300—350 nm 的范围内有吸收,这是产物中 Cl_2 的吸收造成的^[6, 8].

3 小结

用等离子体降解 CF_2ClBr 能生成比它本身毒性更大的 CF_2O 、 Br_2 、 Cl_2 , 要将此付诸实践,还有很多工作要做,主要是降解产物的无毒、无害化处理以及寻找最佳降解条件,这些都还有待深入研究.

参 考 文 献

- 唐孝炎主编. 大气环境化学. 北京: 高等教育出版社, 1990: 55
- 刘正超等. 环境科学, 1996, 17(4): 1
- Shimanouchi T. J. Phys. Chem. Ref. Data, 1977, 6(3): 1061
- Eliasson B & Kogelschatz U. IEEE Trans. Plasma Sci., 1991, 19(6): 1063
- Nielsen A H. J. Chem. Phys., 1952, 20: 596
- [美]冈田秀雄著, 汤国庆等译. 小分子光化学. 长春: 吉林人民出版社, 1982: 218
- 印永嘉主编. 物理化学简明手册. 北京: 高等教育出版社, 1988: 512
- Mishalanie E A et al. J. Phys. Chem., 1986, 90(22): 5578

Isolation of Bacteria for Degradation Benzene Homologue under Aerobic Condition. Lu Jun, Wang Jusi et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 1—4

In order to sift for bacteria of degrading benzene homologue compounds, 25 strains degrading toluene, ethylbenzene, o-, m- and p-xylene and trimethylbenzene were isolated by selective enrichment from activated sludges of petrochemical and municipal wastewater treatment plants. The strain species are able to degrade the benzene homologue compounds as the sole source of carbon and energy. The results indicated that most of the 25 strains have strong capability of biodegrading benzene homologue compounds under aerobic condition.

Key words: benzene homologue compounds, aerobic degradation, bacteria, isolation.

Analysis of Economic Loss from Ecological Deterioration in Typical Ecological Regions and Division Districts of China. Wang Junsan and Cai Xinde (South China Institute of Environmental Sciences, NEPA, Guangzhou 510655); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 5—8

In Order to find out that the expressing situation of various ecological environmental deterioration during the process of economic development at present in China and assessing comprehensively the ecological environmental impact which was made by mankind activities, the method of quantitative and semi-quantitative conversion was applied. The economic loss from ecological deterioration of including Guangdong, Hainan etc. 11 provinces and regions was analyzed and evaluated. Based on the analytic results, the interrelation model and the diagnosis model about economic loss of 11 provinces and regions have been established. The interrelation model and parameters of assessing economic loss can be applied in the similar conditions of ecological environmental and economic development intensity. The economic loss of some regions can be evaluated using the diagnosis model and the amount of various ecological deterioration. The division districts of ecological deterioration of whole country have been made. The basic situation of various districts of ecological deterioration and the distributional characteristics which include the serious deterioration areas and the intensity deterioration areas have been summed up. The proportion of various ecological deterioration areas to national land areas have been calculated.

Key words: ecological deterioration, economic loss, region districts, interrelation model, diagnosis model.

Study on Kinetics of Biofilm Suspension Reactor. Zhou Ping and Qian Yi (Dept. of Environ. Eng. Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 9—12

Study on the liquid circulation velocity, organic matter degradation kinetics and biofilm detachment rate in airlift biofilm suspension reactor was conducted. The results showed that the inner circulation velocity is proportional to the reactor height and the 0.5 power of the superficial gas velocity in the riser. The reactor can be treated as CSTR when inner circulation flux is high. The biofilm detachment rate is proportional to the first power of superficial gas velocity in riser and the biofilm thickness and the 2/3 power of carrier quantity in reactor, respectively. **Key words:** airlift biofilm suspension reactor, inner circulation velocity, organic matter degradation kinetics, dimensional analysis, biofilm detachment rate.

Two-Phase Anaerobic Digestion of Water Hyacinth Pretreated with Dilute Sulphuric Acid. Zhou Yuexi et al. (Chinese Research Academy of Environmental Science, Beijing, 100012); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 13—16

In this paper, diphasic fermentation of water hyacinth pretreated with dilute sulphuric acid was studied. Experimental results demonstrated that specific biogas yield of 134 litre per kilogram fresh water hyacinth was obtained with methane content of biogas about 75.1%. Effluent COD_{Cr}, SS were less than 320 mg/L, 40 mg/L respectively. And microbiological mechanism was also studied.

Key words: water hyacinth, pretreat, two-phase, anaerobic.

Study on Biodegradation of Nonionic Surfactant by Bacteria. Lin Li and Huifeng Yang (Institute of Microbiology, Chinese Academy of Sciences, Beijing 100080), Xia Xinghui and Xu Jialin (Institute of Environmental Sciences, Beijing Normal University, Beijing 100875); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 17—20

Two strains isolated from soil contaminated by petroleum chemicals, *Pseudomonas* sp. strain 52 and *Weeksella* sp. strain 6 could utilize nonionic surfactants (AEO-9 and SA-20) as sole source of carbon for growth. The experiment results showed that the optimum source of nitrogen was ammonium acetate, the optimum pH and temperature for the degradation were 7.0 and 30°C. It was found that addition of glucose enhanced biodegradation of AEO-9. With the initial concentration of 5 000 mg/L the growth cells of the two strains had an AEO-9 removal efficiency of 85% and 95% within 2 weeks or 4 weeks, respectively. The biodegradation rate of AEO-9, in the same initial concentration, by resting cells of strain 52 was 60% within 6.5 hours under the optimum degradation condition in which pH, temperature and cell density (wet weight/volume) was 7.0, 30°C and 20%, respectively.

Key words: *Pseudomonas* sp. 52, *Weeksella* sp. 6, nonionic surfactant, biodegradation.

The Influence of Extra Gases in Degradation of CF₂ClBr

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: $\text{He} < \text{N}_2 < \text{O}_2$, 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 $1.70 \times 10^{-3} \text{ s}^{-1}$ 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 chloroform 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-