含铬废渣炻质砖固体块长期稳定性试验和加速试验*

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摘要 在制砖基料中加入20% 铬渣, 制成所要求几何形试块, 按给定的烧成温度烧成试块, 测量烧成试块几何尺寸及烧成前后试块所含水溶性 Cr(Ⅵ) 值. 将烧成试块置于不同条件的浸出液中进行长期浸取. 根据1a 的浸出数据, 浸出率 $LR = 0.8\times10^{-7}$ cm/d, 累积浸出分数 $LF = 1\times10^{-4}$ cm, 判断炻质砖试块中 Cr(Ⅵ) 的稳定程度, 从而判定此处理铬渣方法的可行性.

关键词 铬渣, 炻质砖, 六价铬, 稳定性.

铬渣是生产金属铬和铬盐产品的主要废渣, 因其含有超量水溶性 Cr(Ⅵ) 而具有毒性. 现处置处理的方法有烧制青红砖法, 炻质砖玻化砖法, 水泥砖蒸养砖法、铸石法、矿棉法、烧结矿法, 着色剂和钙镁磷肥法等. 评价这些方法可行性的先决条件是这些含铬废渣制品中的铬(包括 Cr(Ⅲ), Cr(Ⅵ)) 是否稳定, 是否长期(如1a) 没有"回升"现象. 目前, 我国尚无检测含铬制品长期稳定性方法. 本研究建立了检测含铬废渣炻质砖试块长期稳定性方法, 为含铬废渣炻质铺路砖产品的安全使用提供了科学依据.

1 实验方法

1.1 试块配方及烧成温度

原料配方: 黄土65%, 铬渣20%, 矾渣15%. 原料配方和化学成分如表1.

表1 炻质砖试验样块所用原料化学成分1)

原料名称	灼减/%	化学成分/%							
		SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	CaO	MgO	KNaO
铬 渣	10.32	10.74	0.17	7.76	7.35	4.68	32.22	23.95	2.74
矾 渣	14.79	5.19	3.17	72.40	2.76		0.42	0.10	1.05
黄 土	5.42	69.86	0.82	13.10	4.48		1.42	1.32	3.51

1) 烧成温度为1170℃, 保温3h.

1.2 长期稳定性试验样块制备参数

作长期稳定性浸出试验, 对固化体及浸出剂有一定要求, 固化体可制成圆柱体或长方体; 浸出剂用量大体上超过固化体表面积10倍, 液固比为10∶1为佳.

本次试验共取24块烧制后的圆柱形固化体, 分4组浸泡, 有关参数列于表2.

1.3 水溶性 Cr(Ⅵ) 浸出值的测定

所用样块参数与表1、表2相同. 坯块经1170℃烧成后, 粉碎140目全通过, 依据铬浸出毒性监测分析方法(二苯碳酰二肼光度法) 测量其水溶性 Cr(Ⅵ) 含量, 结果列于表3.

1.4 测量设备及装置

加热装置: E64-1型真空卧式干燥炉; 浸出装置: 图1给出长期浸取所用装置示意图; 图2为索氏法试验装置图; 测试设备: 751型分光光度计.

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表2　长期稳定性试验样块参数

参数	直径/cm	高/cm	表面积 S/cm²	体积 V/cm³	V/S/cm	试块重量/g	A_0[1] ×10³/μg
19-24样块平均值	1.98	1.89	17.89	5.80	0.32	11.41	2.28

1) A_0为烧制前样块中水溶性 Cr(Ⅵ) 浸出值

表3　烧成样块水溶性 **Cr**(Ⅵ) 测量结果[1]

样品号	测试试样量/g	浸出液体积/ml	分析取样体积/ml	消光值/E	Cr(Ⅵ) 浸出值/μg	样品中水溶性 Cr(Ⅵ) 含量/μg·g⁻¹
1	4	50	15	0.068	1.5	1.25
2	4	50	15	0.039	0.8	0.67
3	4	50	15	0.051	1.1	0.92
4	4	50	15	0.039	0.8	0.67
5	4	50	15	0.085	1.9	1.58
6	4	50	15	0.058	1.3	1.08
平均值						1.03±0.35

1) 含铬废渣污染物控制判别标准为5μg/g

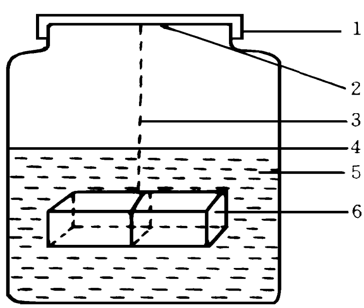

图1　浸出试验装置

1. 外盖　2. 内盖　3. 尼龙丝　4. 聚乙烯罐
5. 浸出剂　6. 含铬烁质砖试样

1.5　长期浸出试验

采用3种边界条件和一种定性方法进行长期浸出试验，即蒸馏水长期浸泡及蒸馏水加温(72±2℃)浸泡、蒸馏酸性水(pH=3)常温浸泡和索格利特法定性浸出试验.

常温、加酸常温和加热长期浸取试验：按计划时间更换浸出液，过量浸出液经蒸发浓缩约100ml 转移到100ml 计量瓶内加水至刻度. 取50ml 测水溶性 Cr(Ⅵ)，另50ml 测 Cr(Ⅵ) 总量(即包括酸溶性 Cr(Ⅵ) 部分).

索氏方法：2台装置同时工作，样品块在装置内被连续加热浸淋，时间为72h，浸淋后的浸出液经蒸发浓缩约100ml，分别测量水溶性 Cr(Ⅵ) 和 Cr(Ⅵ) 总量.

1.6　测试结果

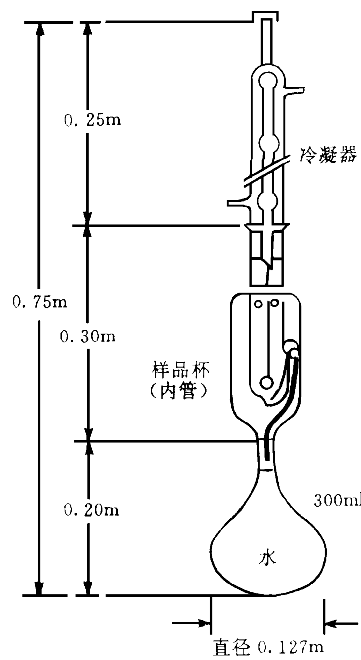

图2　索格利特法试验装置图

根据《放射性废物固化体的长期浸出试验》方法测试长期稳定性参数：

$$\text{Cr 的浸出率 } LR = \frac{a_n}{A_0 \cdot t_n} \cdot \frac{V}{S} (\text{cm} \cdot \text{d}^{-1})$$

$$\text{Cr 的累积浸出分数 } LF = \frac{\sum a_n}{A_0} \cdot \frac{V}{S} (\text{cm})$$

式中，A_0为样块中水溶性 Cr 原始含量(μg)；a_n为第 n 次浸出时间内 Cr 浸出量(μg)；V 为试块体积(cm^3)；S 为试块面积(cm^2)；t_n 为第 n 次浸

出的持续时间(d).

烧制前试块中水溶性 Cr(Ⅵ) 含量为 2000μg/g, 可溶性 Cr 总量为 2600μg/g, 所以,

A_0= 2600μg/g×烧成后试块平均重量(g).

测量结果分别列于表4和表5.

表4　长期浸出试验数据表

浸出时间	t_n/d	1	2	3	4	4	7	7	7	7	30	30	60	91	113
	$\sum t_n$/d	1	3	6	10	14	21	28	35	42	72	102	162	255	366
常温 Cr(Ⅵ)	a_n/μg	0.64	0.54	0.18	0.28	0.39	0.30	0.36	0.49	0.47					
V/S= 0.32	$\sum a_n$/μg	0.64	1.18	1.36	1.64	2.03	2.33	2.69	3.18	3.65					
A_0= 2.26×10⁴/μg	$LR\times10^{-6}$/cm·d^{-1}	9.06	3.54	0.85	0.99	1.38	0.61	0.73	0.99	0.95					
	$LF\times10^{-5}$/cm	0.91	1.67	1.93	2.32	2.87	2.70	3.12	3.69	4.23					
常温总 Cr(Ⅵ)	a_n/μg	0.64	0.56	0.76	0.87	0.62	0.62	0.67	0.66	0.60	0.51	6.96	7.54	8.04	8.92
V/S= 0.32	$\sum a_n$/μg	0.64	1.20	1.96	2.83	3.45	4.07	4.74	5.40	6.00	6.51	0.45	0.58	0.50	0.88
A_0= 2.94×10⁴/μg	$LR\times10^{-6}$/cm·d^{-1}	6.96	3.05	2.76	2.37	1.69	0.96	1.04	1.03	0.93	0.18	0.16	0.11	0.06	0.08
	$LF\times10^{-5}$/cm	0.70	1.31	2.13	3.08	3.75	4.43	5.16	5.88	6.35	7.08	7.57	8.20	8.75	9.71
pH= 3　常温	a_n/μg	0.33	0.25	0.20	0.35	0.36	0.34	0.37	0.33	0.26					
Cr(Ⅵ)	$\sum a_n$/μg	0.33	0.58	0.78	1.13	1.49	1.83	2.20	2.53	2.79					
V/S= 0.32	$LR\times10^{-6}$/cm·d^{-1}	4.65	1.76	0.93	1.23	1.27	0.68	0.75	0.66	0.52					
A_0= 2.95×10⁴/μg	$LR\times10^{-5}$/cm	0.47	0.82	1.10	1.59	2.10	2.58	3.10	3.57	3.93					
pH= 3　常温	a_n/μg	0.62	0.86	1.16	0.38	0.52	0.87	1.10	0.75	0.73	0.70	0.73	0.63	0.57	1.20
总 Cr(Ⅵ)	$\sum a_n$/μg	0.62	1.48	2.64	3.52	4.04	4.91	6.01	6.76	7.49	8.19	8.92	9.55	10.12	11.32
V/S= 0.32	$LR\times10^{-6}$/cm·d^{-1}	6.73	4.66	4.19	2.39	1.41	1.35	1.70	1.16	1.13	0.25	0.26	0.11	0.07	0.16
A_0= 2.95×10⁴/μg	$LF\times10^{-5}$/cm	0.67	1.61	2.86	3.82	4.38	5.33	6.52	7.33	8.12	8.88	9.68	10.36	10.98	12.28
70℃ Cr(Ⅵ)	a_n/μg	0.83	0.87	0.5	0.4	0.49	0.31	0.44	0.41	0.48					
V/S= 0.32	$\sum a_n$/μg	0.83	1.70	2.20	2.60	3.09	3.4	3.84	4.25	4.73					
A_0= 2.27×10⁴/μg	$LR\times10^{-6}$/cm·d^{-1}	11.70	6.13	2.35	1.41	1.73	0.62	0.89	0.83	0.97					
	$LF\times10^{-5}$/cm	1.71	2.40	3.10	3.67	4.36	4.79	5.41	5.99	6.67					
70℃总 Cr(Ⅵ)	a_n/μg	0.94	0.95	0.52	0.7	0.54	0.50	0.53	0.54	0.47	0.63	0.88	0.45	0.50	0.47
V/S= 0.32	$\sum a_n$/μg	0.94	1.89	2.41	3.11	3.65	4.15	4.88	5.22	5.69	6.32	7.20	7.65	8.15	8.62
A_0= 2.95×10⁴/μg	$LR\times10^{-6}$/cm·d^{-1}	10.20	5.15	1.88	1.90	1.46	0.77	0.82	0.84	0.73	0.23	0.32	0.08	0.06	0.05
	$LF\times10^{-5}$/cm	1.02	2.05	2.61	3.37	3.96	4.50	5.08	5.66	6.17	6.86	7.81	8.30	8.84	9.35

表5　索氏测试 **Cr**(Ⅵ) 浸出量

样品号	消光值	Cr(Ⅵ) 浸出量/μg	Cr(Ⅵ) 含量/μg·g^{-1}
1	0.001	0.4	0.035
2	0.011	0.4	0.035
3	0.027	1.2	0.104
4	0.011	0.4	0.035
5	0.013	0.6	0.053
6	0.029	1.3	0.113
平均值		0.72±0.42	0.063

由表5平均值看出, 样块中经72h 的铬浸出量为: 0.063÷2600= 2.4×10^{-5}.

测量结果表明: 采用笔者配制的原料配比, 经过1170℃烧成并保温3h 的样块, 其铬含量是很稳定的, 使用沸腾水浸淋的索氏法测试3d, 其浸出量仅为原值的2.4×10^{-5}. 经过常温、加温、酸性浸出液浸取1a, 铬仍以稳定形态存在, 其浸出率在1×10^{-6}(cm/d) 量级, 累积浸出分数在1×10^{-4}(cm) 量级.

2　应用领域及效果

本试验方法可广泛应用于铬盐行业、铬金属生产行业和揉革行业中含铬废渣、含铬铝泥综合处置处理的监测与评价, 获得明显的经济、社会和环境效益.

Viaduct. Chen Ziming (Department of physics, Ocean University of Qingdao), Liu Weiming et al. (Environmental Monitoring Centre, Qingdao): *Chin. J. Environ. Sci.*, **18** (3), 1997, pp. 41_ 44

The popular response to the traffic noise of elavated highway or viaduct in the Qingdao City was investigated using simultaneous doing method of questionaires and noise measurements. The variations of subjective annoyance value and sleep interference rate with the effective noise level was analysed. The difference in the subjective annoyance values and sleep interference rates of population of different groups was pointed out and the difference in their subjective response before and after the construction of an elevated highway or viaduct.

Key words: traffic noise, elevated highway or viaduct, subjective response, subjective annoyance value, sleep interference.

Reformed Methane by Carbon Dioxide over Co/Al_2O_3 Catalyst. Fei Jinhua, Lu Haihua et al. (Institute of Catalysis, Hangzhou University, Hangzhou 310028): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 45_ 46

In this paper, the effect of Co content, pretreatment conditions, space velocity and reaction temperature on the preformance of mathane reformed to synthesis gas by carbon dioxide over Co/Al_2O_3 catalysts has been investigated. It was found that Co/Al_2O_3 catalyst with Co content of 13% (wt) (i.e. 13% wtCo/Al_2O_3) showed the best reform activity, decreasing space velocity and increasing reaction temperature improved the conversion of mathane and carbon dioxide. Catalysts also showed the best activity at reduced temperature at 400℃. The CO/H_2 ratio of yieids increased with the space velocity increasing, decreased with reduced temperature and reaction temperature increasing. When enough Co content is loaded on Al_2O_3(eg. 13%wtCo/Al_2O_3), catalysts will appeare longer life and stability of activity.

Key words: mathane, carbon dioxide, synthesis gas, catalyst, reform, Co/Al_2O_3.

Basic Study on Neural Active Noise Barrier of Distributed & Coordinated Multi-Channels. Chengxiang Tan and Songling Zhao (The Institute of Acoustics, Tongji University, Shanghai 200092): *Chin. J. Environ, Sci.*, **18** (3), 1997, pp. 47_ 49

The height, material, architecture, weight of the noise barrier are constrained by the landscape requirement and load-bearing frame, which deepens the deficiency of the conventional noise barrier in low frequency wide band noise diffraction and transmission. To improve the performance of the conventional noise barrier, neural active noise barrier of distributed and intelligently coordinated multichannels is presented. The adaptive nonlinear control vector in time and space domains is self-organized by the proposed compound neural network to drive the distributed secondary sources array optimized. Multiobjectives optimization is adopted. Through training, at first, the neural network optimizes the geometrical distribution of the sensors and secondary sources, in order to synthesize the suitable noise reducing space distribution and reduce the hardware cost; secondly, the structure of the neural controller is simplified. At last, the reserved connection weights get precisely optimized. The scheme is demonstrated to be applicable especially for wideband and large area noise barrier.

Key words: noise control, noise barrier, neural network.

Chinese Expressway Tunnel Pollution and Control. Wany Mingnian, Wong Hanmin, Guan Baoshu (Dept. of Underground Engineering, Southwest Jiaotong Universty, Chengdu 610031): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 50—53

In order to control air pollution and noise pollution in expressway Tunnel, i.e. Zhong Liangshan Tunnel、Wu Tongshan Tunnel and Qi Daoliang Tunnel were studied, the site test result showed that machinery ventilate control effectively air pollution in tunnel, source of noise is traffic flow, their noise go beyond the values of standard, so it is important to study on technique reduced noise pollution.

Key words: expressway tunnel, air pollution, noise pollution, machinery ventilate.

Experiments on Long Term Stability of Road Tile Made from Chromium-Bearing Slag. Wang Yongzeng et al (China Institute for Radiation Protection. Taiyuan 030006): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 54_ 56

By adding 20% chromium-bearing slag into base materials of making brick, the brick sample was sintered in the required geometric shape under the given temperature. The size of sintered base sample was measured and the associated Cr water solubility test made before and after sintering. The sample was tested in leaching liquid under variable conditions. Based on the experiment results data, the leaching rate is 0.8×10^{-7} cm/d and the accumulative leaching faction is 1×10^{-4} cm/d, the stability of Cr in base sample was determined and therefore such method of treating chromium slag was considered feassible and practible.

Key words: chromium-bearing slag, road tile, stability.

Study on Effects of Developing Touristry for Songshan Conservation Area. Song Xiujie and Zhao Tongrun (Beijing Municipal Research Academy of Environmental Protection, 100037): *Chin. J. Environ. Sci.*, **18** (3), 1997, pp. 57_ 59

In order to evaluate effect of touristry development for Songshan Conservation Area, the investigating site and monitoring water, quality which include surface and underground water, and atmospheric quality were carried out. It was found that the natural landscape of the conservation area was destroied lightly because of trampling, picking and throwing by tourists and touristry facilities established, but quality of surface water and underground water are fit for National Standard. Atmospheric pollutants are fit for First National Standard. Need to strenthen management of the conservation area was suggested.

Key words: Songshan Conservation Area, environmental effect, touristry development, management.

Effect of Calcium on Cell Membrane Permeability in Acid Rain Stressed *Cucumis melo* Seedling. Zhou Qing and Huang Xiaohua et al. (Dept. of Biology Suzhou Railway Teachers College, Suzhou 215009): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 60_ 61

The relationship of calcium to cell membrane permeability in acid rain stressed *Cucumis melo* seedling has been studied. Calcium obviously decreased cell membrane permeability and protected cell membrane from acid rain insult. Optimum protection effect is that *Cucumis melo* seedling is spraied continuously two times (once every 24 hours) with concentration of 30mmol/L $Ca(NO_3)_2$ at the test conditions. The mechanism perhaps is calcium reagent stabilizing the structure of cell membrane of *Cucumis melo* and raising catalase activity.

Key words: *Cucumis melo* seedling, cacium, cell membrane permeability, acid rain stress.

Spectrophotometric Determination of Manganese with Diantipyryl-(P-Bromo)-Phenylmethane. Yin Jiayuan and Yang Guangyu et al. (Department of Chemistry, Yunnan University, Kunming 650091): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 62_ 63

Diantipyryl-(p-bromo)-phenylmethane (DApBM) was synthesized and indentified. A highly sensitive spectrophotometric method has been developed for the determination of manganese with DApBM. In the presence of Mn(Ⅱ), Mn(Ⅶ) can reacts with DApBM to form an orange and yellow product in phosphoric acid mediun. The molar absorptivity is 1.28×10^6 L·mol^{-1}·cm^{-1} at 480nm. Beer's law is in keeping in the range of 0.1－0.9μg/25ml. This method has been applied to the determination of manganese in food and water, the results are satisfactied.

Key words: diantipyry-(p-bromo)-phenylmethane, spectrophotometric, manganese.

Determination of CH_3SH in Air Using Capillary GC/FID. Wang Lizhong, Lu Yongsen et al. (Key State Lab. of Pollution Control and Resources Reuse, School of Environ. Eng., Tongji University, Shanghai 200092), Wang Wenling (Department of Chemistry, Fudan University, Shanghai 200433): *Chin. J. Environ. Sci.*, **18**(3), 1997, pp. 64_ 66

The analytical procedure for methylmercaptan in air was investigated which involves four phases of sampling, low temperature concentration with liquid nitrogen, thermal separation and then capillary column GC/FID analysis. Under the conditions selected, a method linear range of 0.2－200 ng was obtained with a minimal detection limit of 0.2 ng. The recovery was about 92.6% with a relative standard deviation of 3.2%. This Procedure was applied to determine the concentration of methylmercaptan in the environmental air around a waste water plant and a polluted river successfully. The odour strength of the air at different sampling points was also calculated, and the distribution characteristic with methylmercaptan sounded reasonable.

Key words: methylmercaptan, GC/FID analysis, sampling, malodor.

Progresses of Bioremediation Studies and Applications. Lin Li and Yang Huifang (Institute of Microbiology, Chinese Academy of Sciences, Beijing 100080): *Chin. J. Environ. Sci.* **18**(3), 1997, pp. 67_ 71

A review concerns principles and techniques on degradation of xenobiotics and recalcitrants in contaminated site. The basic principle of bioremediation that for special contaminated site different treatment techniques were selected on three factors which are decrease the toxicity of pollutants and increase the bioavailibility of pollutants and the bioactivity of microorganisms. The recently advances at in-situ and ex-situ bioremediation techniques are involved in the paper which include adding nutrient, inoculate species, bioventing, landfarming, comporting piles, biopiles and slurry techniques. The methods of collecting the site information and of evaluating treatment were discussed also.

Key words: bioremediation, contaminated site, xenobiotics, recalcitrants, microorganisms, bioavailibility, bioactivity.

Advances in the Study of Remediation Methods of Heavy Metal-Contaminated Soil. Xia