治理技术

煤矸石-粉煤灰-废石膏烧结陶粒*

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摘要 采用制粒烧结工艺成功地把煤矸石、粉煤灰及废石膏(或烟气脱硫污泥)制备成建筑用轻质陶粒，实现了对上述固体废物的资源化和稳定化。煤矸石等的配料比以及粉状原料的颗粒尺寸分布是在成球盘中制粒的主要影响因素。烧结过程中的影响因素较多，但烧结温度是影响产品质量的主要因素。煤矸石-粉煤灰-废石膏陶粒烧结过程发生在950—1250℃，最佳烧结温度为1200±50℃，制得的陶粒坚硬如岩石，容重等级为900，筒压强度为9—15 MPa，超过GB2838-81的筒压强度≥6.5 MPa的规定。

关键词 陶粒，煤矸石，粉煤灰，烟气脱硫污泥，综合利用。

煤矸石和粉煤灰是我国能源生产和使用过程中产生的2大固体废弃物。除此之外，烟气脱硫污泥将是我国潜在的数量巨大的固体废物。随着我国火电厂烟气脱硫装置的逐步建造，这类以二水硫酸钙为主要成分的污泥的处理将成为一大环境问题[1]。利用煤矸石或粉煤灰制作建筑用陶粒国内外已有广泛的研究[2-5]，但用煤矸石、粉煤灰和烟气脱硫污泥3种原料来制备烧结陶粒的报道却很少。而这种制备工艺对处理和利用上述废渣更为全面和更为实用。由于烟气脱硫污泥在我国数量暂时还不大，在本研究中以废石膏代之。该废石膏来自用石灰石中和硫酸废水而产生的废渣。

1 材料与方法

1.1 原材料

(1) 煤矸石 试验用煤矸石分别取自山西省霍县矿务局，江西省萍乡矿务局和云南省华坪煤矿。它们的化学组分及热值等列于表1。

(2) 粉煤灰 取自上海吴泾热电厂。外观呈灰色，颗粒较细。颗粒的重量平均直径约0.1 mm。粉煤灰的组成与性质因电厂所燃煤种和燃烧工况不同而差异较大。试验用粉煤灰是由2份大同煤与1份平顶山煤混合后燃烧所得。吴泾热电厂粉煤灰的化学组成与热值也见表1。

(3) 废石膏粉 取自上海染料化工厂石灰法处理硫酸废水得到的泥浆，经干燥磨细后使用，呈灰黑色。其化学组成见表1。

1.2 烧结陶粒的制备方法

陶粒的制备工艺过程为：

煤矸石
粉煤灰 →配比→粉碎混合→制球→干燥
废石膏 ↓
性能测试←高温烧结

表1 几种原料的化学组成及性质

原 料	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	$CaSO_4$ (%)	LOI[1)] (%)	热值 (kJ/kg)
霍县煤矸石	28.30	22.94	4.57	1.57			42.38	15380
萍乡煤矸石	59.73	18.39	1.31	0.25	1.26		18.8	5420
华坪煤矸石	69.57	12.96	3.92	0.31	1.86		6.5	1680
吴泾粉煤灰	54.35	32.72	6.43	2.25	0.91		4.7	1110
废 石 膏	2.17	9.39	1.23			86.53	19.8	0

1) LOI为烧失量

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几种原料经重量配比后在球磨机中磨细并混合，通过26目筛子并弃去筛上物。制球所用的设备是成球盘，它由孛荠式糖衣机改制而成。圆盘的直径为0.8 m，盘的边高为14 cm。转盘的转速为32 r/min。圆盘的倾角可在42°－60°之间任意调节。电机功率为1.1 kW。混合物料不断地加入到转盘内并不断喷水。粉状物料在转盘中经历母球的形成和球粒增大并密实2个阶段后逐渐形成具有一定机械强度的生料球。当生料球的直径增大至一定尺寸后会从成球盘中自动跳出。实验中控制生料球的直径在10－20 mm。

采用ASTM D440-49重复坠落未破损率(%)或跌落破碎平均次数法测定生料球的机械强度[2]。生料球强度视为满意的测定指标如下：ASTM D440-49方法测定时，坠落未破损率≥90%。以跌落破碎平均次数法测定时为平均跌落15次以上不破碎。实验发现，用上述2种方法测定生料球机械强度时，测定结果基本上是一致的。因跌落破碎平均次数法测定比较简便，在本实验中较多采用。

生料球经120℃烘干后，在电炉中进行焙烧。达到烧结温度后，一般保持恒温40 min。然后切断电源，在空气中冷却，制得坚硬的烧结陶粒。

陶粒的筒压强度按GB2842-81标准由上海建筑科学研究所测定。

2　结果与讨论

2.1　生料球的制备

2.1.1　物料的粒度分布对制球的影响

煤矸石经破碎、球磨并通过26目的筛子过筛后再用筛析法测出它的平均粒径(实际上是重量平均粒径)。试验用的煤矸石粉的平均粒径$d_m=0.292$ mm。这种粒度分布的粉末在成球盘中很易成球。在上述粉料中有意地加入一定重量的0.71－1.26 mm的大颗粒煤矸石粉，再制球并测定生料球的机械强度，其结果见表2。

表2　粉末颗粒级配对生料球强度影响

项　目	煤矸石粉末中含0.71－1.26 mm颗粒的比率(W%)			
	10	20	30	40
ASTM重复坠落未破损率(%)¹⁾	98	96	95	无法成球
跌落破碎平均次数²⁾	>30	>20	>20	无法成球
颗粒重量平均粒径(μm)	361	431	500	569

1) 取50 g生料球样品，从1.2 m高处重复坠落3次，颗粒碎片用6目筛子过筛，计算出筛上物所占的重量百分数为未破损率；2) 约10个生料球分别于0.6 m高处反复跌落到一个坚硬的平板上，直至发生破碎，记录跌落次数，计算平均跌落破碎次数。

试验表明，当煤矸石粉末中粗粒子(0.71－1.26 mm)的重量占40%时，不能成球。其它试验表明，若粒径为0.71－1.26 mm的颗粒重量占30%而颗粒的平均粒径达到830 μm时，它们在成球盘中也难以成球。因此粉状物料的颗粒尺寸分布和颗粒级配是制球工艺中的一个重要的影响因素。

2.1.2　煤矸石和粉煤灰混合比的影响

不同重量比的煤矸石粉末(以下简称矸)和粉煤灰(以下简称灰)对生料球强度的影响见表3。

表3　矸/灰重量比对生料球强度的影响

矸/灰重量比	1∶1	3∶2	2∶1	3∶1	∞
跌落破碎次数	<5	9	9.5	≥15	≥20

表3结果表明，为满足生料球的跌落破碎次数≥15，矸与灰的重量比应≥3。这是因为经历了高温灼烧的粉煤灰与水的粘结性较差，不添加粘结材料直接与水混合制球是比较困难的。一般讲，煤矸石粉与水的粘结性较好。从表3结果可看出单独煤矸石粉与水混合能很好成球且生料球的机械强度也好。在煤矸石粉中混入粉煤灰后，生料球的机械强度下降，混入的粉煤灰越多，生料球的强度越差。

当矸灰比保持为3，逐步添加废石膏粉(以下简称膏)使矸∶灰∶膏分别为3∶1∶0.25，3∶1∶0.5，3∶1∶1和3∶1∶1.5时，它们均能在成球盘中直接成球，其跌落破碎次数≥15。因此制球时控制三者的重量比是重要的。

2.1.3　生料球中含水率的影响

生料球的含水率与机械强度的关系见图1。

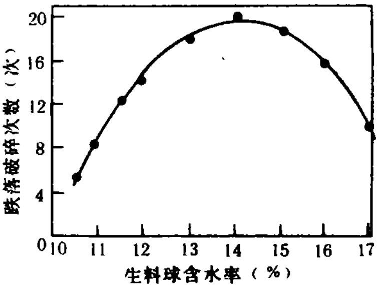

图1 生料球的机械强度与含水率的关系

含水率过低自然不易成球。含水率超过16%时，生料球的强度就不足，同时球粒会粘附在成球盘的盘边处影响正常操作。因此较佳的含水率在12%—16%(*W*/*W*)。

2.1.4 影响制球的其它因素

成球盘的倾角范围为45°—55°。倾角过小，物料会在转盘内滑动而不易成球。倾角超过55°球径变小且易弹出盘外。

圆盘直径和旋转速度对制球也有影响。一般讲，盘子直径小成球较困难。总之，设备条件的差异会给制球工艺参数造成不同的影响。

2.2 烧结试验

2.2.1 原料中含碳量和烧失量的影响

用霍县煤矸石与粉煤灰制成的生料球经高温烧结的陶粒发现其抗压强度都非常低。究其原因是煤矸石中含碳量过高。改用烧失量与热值都较小的华坪煤矸石，以矸∶灰为3∶1，再混入炭粉来改变料球中的LOI，使LOI分别为6.3%，9.1%，12.6%，14.2%和18.7%。经成球和烧结后，测出陶粒的颗粒抗压力，结果见图2。

图2可见，陶粒的抗压强度随LOI的增加而下降。根据GB2838-81，容重等级为900的陶粒其筒压强度应≮6.5 MPa。后文将会说明对应于筒压强度6.5 MPa的单颗抗压力则为480 N。从图2得出要使陶粒满足强度指标，生料球的LOI≯10%，含碳量≯10%。这与文献报道的含碳量取5%—10%为宜相一致。煤矸石中含碳量高则可利用的热值也高，可节省外加的能量。但含碳量或烧失量过大会影响陶粒的质量。

2.2.2 烧结温度的影响

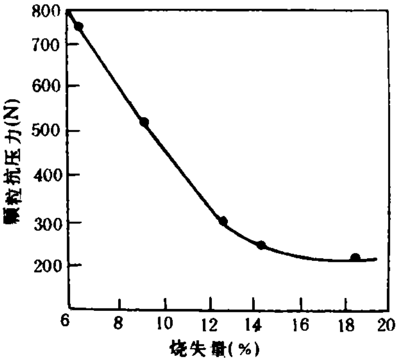

图2 陶料的抗压力与烧失量的关系

烧结温度 $t=1050$℃

陶粒的筒压强度与焙烧温度的关系如图3所示。陶體的强度随焙烧温度的升高而逐渐增大并在某一温度范围内迅速上升至最大值。

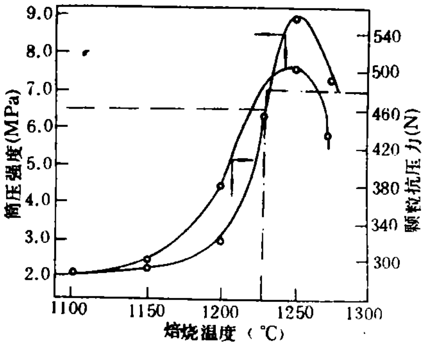

图3 陶粒的抗压强度与烧结温度的关系

萍乡煤矸石∶粉煤灰∶石膏＝3∶1∶0.5

图3还表示了单颗陶粒的抗压力与焙烧温度的关系。2条曲线有类似的变化规律。对应于筒压强度为6.5 MPa的颗粒抗压力则为480 N(对应的烧结温度为1220℃)。因为测定颗粒的抗压力所需样品少，测试简便，在有些试验中以颗粒的抗压力作为陶粒性能的指标以代替筒压强度。

2.2.3 物粒配比的影响

以华坪煤矸石、粉煤灰、废石膏组成的二元或三元陶粒中，它们不同质量配比时陶粒的抗压力与焙烧温度的关系见图4。

图4的曲线形状与图3是相似的。但物料配比不同，出现峰值的烧结温度是不同的。若把出现最大颗粒强度时的温度取作 T_S，则单纯

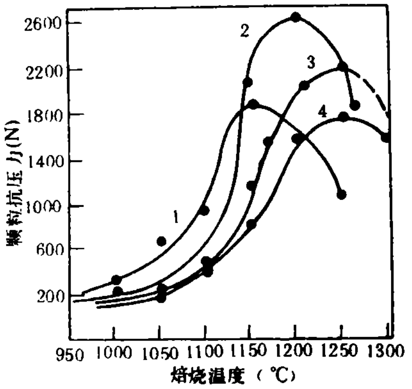

图4 不同石膏含量的颗粒抗压力与焙烧温度的关系

1. 矸：灰：膏＝3：1：0 2. 矸：灰：膏＝3：1：0.5

3. 矸：灰：膏＝3：1：1 4. 矸：灰：膏＝3：0：0

煤矸石的T_S最大。加入粉煤灰后T_S降低。在煤矸石与粉煤灰中再加石膏，那么随石膏量的增多T_S增大。

若煤矸石与粉煤灰的质量比固定在3：1，逐步增加废石膏在陶粒中的含量使矸：灰：膏分别为3：1：0.25，3：1：0.5，3：1：1，3：1：1.5。并固定最高焙烧温度为1150℃，陶粒的筒压强度与石膏含量的关系见图5。由图5可知，随着石膏含量的增加，陶粒强度下降。但是陶粒的颗粒容重一般随石膏含量的增加而减少。而且陶粒的抗压强度仍然很大，大于国家标准规定的指标，这可从表4看出。

表4 1150℃烧结时不同配比陶粒的主要性能参数

质量配比(矸：灰：膏)	3：1：0	3：1：0.25	3：1：0.5	3：1：1	3：1：1.5
松散容重(kg/m³)	990	895	925	828	818
颗粒容重(kg/m³)	1660	1650	1490	1481	1240
吸水率(%)	9.5	4.5	20	19.6	8.9
筒压强度(MPa)	15	15.5	11.4	10.1	8.7
粒径范围 (mm)	10—20	10—20	10—20	10—20	10—20
陶粒外观	灰褐色	褐色	棕黑色	棕黑色	黑色，表面釉化内部发泡

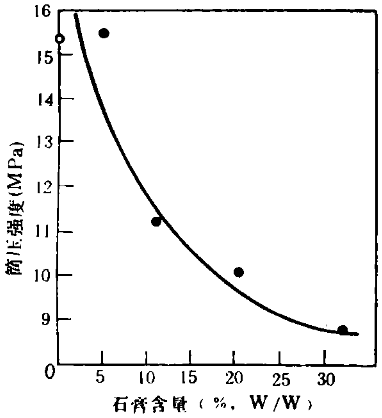

图5 陶粒的筒压强度与石膏含量的关系

烧结温度1150℃，矸：灰＝3：1

2.2.4 恒温时间的影响

烧结时延长恒温时间有利于陶粒强度的增加，但增加量不大。结果如图6所示。在烧结温度下，陶粒内部发生着多种固液相反应形成“点焊”结构。但这种反应发生较快，迅速形成玻璃体，因此恒温时间的影响不是很大。操作过程中采取恒温40 min是合理的。

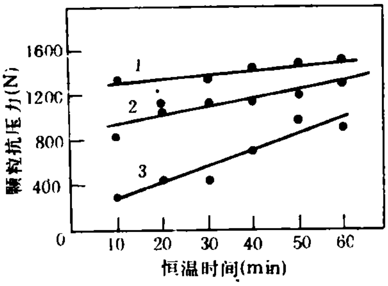

图6 陶粒的抗压力与恒温时间的关系

1. LOI＝9.1% 2. LOI＝12.6% 3. LOI＝18.9%

烧结温度为1100℃

3 结论

（1）通过粉碎、制球和烧结过程可将煤矸石、粉煤灰、废石膏(或烟气脱硫污泥)制成建筑用陶粒。其机械强度满足GB2838-81的要求。该制备过程既是3种工业废渣的稳定化过程又是综合利用的过程。

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min至24 h内的试验结果表明，浸泡10 min催化剂活性即已恢复至最大，故浸泡时间选用15 min。对催化剂再生过程中汞的物料平衡试验结果如表3所示。将浸泡15 min后进入HCl溶液的汞量与催化剂上残留汞量之和作为回收汞量，并将其与催化剂上汞总量之比作为回收率。6次试验结果的平均回收率为99.07%。

2.8　工厂试样的试验

对各种类型工厂排放的含汞废水按取样要求作适当处理，以防止汞的损失。然后测定其汞含量，并进行试验，结果列于表4。表4表明，采用本方法对于5种工厂排放的含汞废水进行治理能获得满意的效果。

表4　5种工厂排放的含汞废水试验结果

废水来源	废水组成			含汞量(mg/L)		汞去除率(%)[1]
	pH	悬浮物(mg/L)	主要成分	处理前	处理后	
化学试剂厂	6—9	60—300	Fe^{3+}、Cl^-、PO_4^{3-}、SO_4^{2-}	60	0.047	99.92
氯碱厂	9—12	25—94	Cl_2、Na^+、OH^-	12	0.0002	>99.99
聚氯乙烯厂	3	500	COD、S^{2-}、C_2H_2	14	0.0004	>99.99
蓄电池厂	14	56	Zn^{2+}、Mn^{2+}、Cl^-	21	0.0005	>99.99
造纸厂	12	850	BOD、Na^+、S^{2-}、CO_3^{2-}	0.2	0.0002	99.90

1）汞去除率系3次以上试验结果的平均值

3　结论

在本方法所确定的治理可溶态汞的适宜条件下，即采用1 g 200目以下的TC5型钛系催化剂（自制），对于含汞量为50 mg/L的试液，经过一次性处理，并控制试液pH为7.5，搅拌时间2 min，可使试液中汞含量下降至0.00044 mg/L，计算出汞去除率达99.99%以上；催化剂经重复多次使用，仍然具有较高的活性，经再生操作后，其活性基本得到恢复；本方法所需设备简易，可在中性或微碱性介质中进行操作，具有实际应用前景。

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（2）原料性能不同对陶粒的质量有较大的影响。3种原料配比不同对陶粒的质量也有影响。

（3）影响制球的主要工艺参数是粉末的粒度分布和煤矸石与粉煤灰的混合比。影响烧结的主要工艺参数是烧结温度。陶粒强度随焙烧温度升高而增强并达到最大值。温度再升高陶粒强度反而下降。不同原料配比存在不同的最佳烧结温度。对于煤矸石-粉煤灰-废石膏3元陶粒而言，最佳烧结温度在1200±50℃。

（4）煤矸石中含碳量不宜过高，否则烧结陶粒的强度不高。一般生料球中含碳量以不超过10%为宜。

（5）石膏含量增加陶粒强度下降，容重也下降。适当的石膏含量可使陶粒具有足够的机械强度。

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lished along with a discriminatory analysis and a multiple non-linear regression analysis. Rates of qualitative discriminatory analysis were not less than 83. 33%. The correlation indices of quantitative regression models (R^2) were over 0. 81. Residuals showed the normal distribution. Predicted values LD_{50} by the regression equations were within a 95% confidence interval of observed values.

Key words: information theoretic indices, valence molecular connectivity indices, structure-toxicity relationship, organophosphorus pesticides, prediction of toxicity.

Design and Implementation of the Jiangsu Province's Environmental Information System. Cheng Shengtong et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 15—18

The objects of Jiangsu Province's Environmental Information System (JSEIS) project and the implementation of the first phase of the project were discussed, the development procedure, hardware, software and network environment were also presented. The process of JSEIS development includes the data normalization, the design of unified data collection report system, the establishment of a basic database for data sharing and a applied database for each of 13 environmental management subsystems developed, the data exchange system among different database products and the data communication at both provincial and municipal levels. The JSEIS allows the data to have integrity, consistency and good practicality.

Key words: environmental management, environmental information system, database management systems.

Remote Sensing Investigation on the Ground Thermal Field and Its Influence on Air Pollution in an Industrial and Mining City. Sheng Yehua et al. (Dept. of Mining, China Univ. of Mining and Technology, Xuzhou 221008): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 19—22

In Jincheng City, Shanxi Province, the two temporal thermal infrared images were taken by means of airborne thermal infrared scanner in early morning (from 5 : 30 to 6 : 30) and midday (from 13 : 30 to 14 : 30) in winter. With reference to simultaneous ground radiation temperature data, some of digital image processing methods, such as image quantization, geometric correction, and thermal field classification, were used for discovering the ground thermal field intensity in the city. Based on these, it was concluded that there is a very obvious ground thermal island effect in early morning and a vague one in midday, and the ground radiation temperature differences for both of the two tempral phases are about 10℃. In addition, the linear relationship between the low altitude air temperature and the ground radiation temperature were computed, and a bad influence of the ground thermal filed on air pollution was found.

Key words: thermal infrared remote sensing, ground thermal field, air pollution.

Identification of Oils Spilt at Sea Surface Based on a Fuzzy Similarity Preference Ratio. Xu Hengzhen et al. (Institute of Marine Environ. Protection, State Oceans Administration, Dalian 116023): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 23—27

A model based on a fuzzy similarity preference ratio has been established to identify different kinds of oils spilt at sea surface, by introducing a concept of the fuzzy area of confidence level λ of a fuzzy similarity preference ratio. The identification of oils spilt at sea surface was found being largely influenced by kinds of oils, experimental errors, and weathering of oils. A Renqiu crude oil after a 30 days weathering was found to have an identifiable confidence level of fuzzy similarity preference ratio in the range of 0. 005819 to 0. 04641 making it different from other 13 kinds of oils. A Daqing crude oil after a 28 days weathering at sea surface was found to have such an identifiable confidence level in the range of 0. 1101 to 0. 2510 inclusive making it different from other 5 kinds of oils. The results from the actual identification of oils spilt at sea surface show that the present method was more precise than a fingerprint spectrograms-based identification method.

Key words: fuzzy, similarity preference ratio, identification, oil spill.

Production of Sintered Ceramsite from Coal Gangue, Fly Ash and Waste Gypsum. Sheng Zhaoqi et al. (Dept. of Environ. Eng., East China Univ. of Technology, Shanghai 200237): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 28—31

A lightweight construction aggregate was suc-

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cessfully manufactured by a granulation and sintering process from coal gangue, fly ash, and waste gypsum or sludge from flue gas desulphurization, which are the principal sources of solid wastes from coal combustion. Formation of green granules and their durability were affected basically by both the mixture partition and the particle size distribution of the wastes when water was added only as a binder in a pan agglomerator. Temperature was the most important factor in the sintering process, though the others could also affect the quality of the aggregates. Granules were sintered at a temperature in the range of 950—1250℃ and the highest compression strength of the sintered ceramsite occurred at a temperature of 1200±50℃ for the coal gangue/fly ash/gypsum granules. The products had a very high strength exceeding the national standard (GB2838-81 specification). The granulation and sintering process was found to achieve the purpose of utilization and stabilization of coal combustion solid wastes.

Key words: ceramsite, coal gangue, fly ash, flue gas desulphurization sludge, utilization of wastes.

Removal of SO$_2$ from Flue Gas by Mn^{2+} Catalytic Oxidation. Chen Zhaoqiong et al. (Dept. of Chem. Eng., Xiangtan Univ., Xiangtan 411105): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 32—34

In order to develop a low price and highly efficent process, the mechanisms and processes for removal of SO$_2$ from flue gas by Mn^{2+} catalytic oxidation have been studied. The results show that the optimum conditions for the processes are pH 5—6 and the Mn^{2+} concentration of 0.06—0.13 mol/L. The use of limestone to neutralize H$_2$SO$_4$ in the absorbing solution may keep a high absorbing efficency and produce the by-product gypsum. In comparison with traditional limestone method, it may avoid scaling on the walls of equipment and slugging, and may not need a oxidation process for producing gypsum. For these reasons, there is a low investment in equipment and a low operation cost.

Key words: flue gas, desulphurization, manganese ion, catalytic oxidation.

New Method for the Efficient Removal of Soluble Mercury from Wastewater. Ye Yuhan et al. (Dept. of Chem., Ningbo Normal Univ., Ningbo 315020): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 35—38

A new process for efficiently removing soluble mercury from wastewater has been developed by using a TiO$_2$/CoO (TC) catalyst developed by the authors. The TC catalyst was stirred with wastewater to be treated at pH7.5 for 2 min, allowing the concentration of mercury in wastewater to be reduced from initial 50 mg/L to final 0.00044 mg/L. The TC catalyst can be repeatedly used, and can be regenerated by HCl if its activity has been reduced to a certain extent. This process has been applied to the treatment of five different wastewaters containing soluble mercury from factories, giving satisfactory results.

Key words: soluble mercury, wastewater treatment, catalyst.

A Pilot Study on the Treatment of Starch Wastewater with Photosynthetic Bacteria. Wang Yuxin et al. (Microbiology Institute, Shandong Univ., Jinan 250100): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 39—40

A strach wastewater was continually treated with photosynthetic bacteria under the optimum conditions in a pilot plant with a treating capacity of 4 m^3 wastewater per day, a maximum COD volume load of 6.71 kg/(m^3 · d), and a COD removal rate of 95.7%. Not only can the pollution of wastewater be eliminated effectively but the bacterial mud can also be used as an important source of feed additive.

Key words: photosynthetic bacteria, wastewater treatment, removal rate of COD, COD volume load.

Preparation of a New Coagulant-FAS and a Study on Its Properties. Wu Qifan and Kong Qingan (Dept. of Applied Chemistry, South China Univ. of Technology, Gangzhou 510641): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 41—43

A process for preparing a new decoloring coagulant-FAS from copper slag was developed. The results show its superior properties for removing turbidity, sulphur, color and COD. Especially, for those hydrophilic dyes which couldn't be well removed by conventional coagulants, FAS has a special ability to remove them. The removal rates of color and COD are over 95% and 90%, respectively. The decoloring mechanism of dyes was found to be mainly through forming their coordination compounds with metal ions in FAS.

Key words: coagulant, dyeing wastewater, decoloring mechanism.