

# 用煤矸石制备聚合氯化铝铁絮凝剂的研究

高宝玉\* 于 慧 岳钦艳 王 艳 黄 佑

(山 东 大 学 环境工程系, 济南 250100)  
山东省环境保护局

**摘要** 为了探讨从煤矸石中浸出铝铁的原理和工艺, 利用透射电镜、红外光谱和 X-射线衍射分析技术对 PAFC 的结构进行了表征, 试验了 PAFC 处理实际工业废水的效果. 结果表明, 用煤矸石制取 PAFC 是可行的; 制备出的 PAFC 是聚合铝铁的复合产物; 用 PAFC 处理煤矿矿井废水及油田含油污水, PAFC 投量为 40 mg/L 时, COD 去除率, SS 的去除率以及除油率分别为 80%, 90% 和 90% 左右.

**关键词** 煤矸石, 聚合氯化铝铁絮凝剂, 水处理.

聚合氯化铝铁(PAFC)是铝铁的复合产物, 它兼有铝盐类和铁盐类絮凝剂的特性, 具有优良的净水性能和广泛的应用范围. 煤矸石是采煤过程的废弃物, 我国历年来积累了大量的煤矸石, 污染环境和占用大量土地, 因此应积极开展煤矸石的综合利用研究. 本研究利用煤矸石中的  $\text{Al}_2\text{O}_3$  和  $\text{Fe}_2\text{O}_3$  成分, 并加进去一定量的铁矿石, 采取一定的工艺条件, 制备出了 PAFC 产品, 并对 PAFC 的结构特征进行了分析, 考

察了 PAFC 处理实际废水的效果.

## 1 PAFC 絮凝剂的制备

### 1.1 煤矸石化学成分分析

煤矸石取自山东省兖州矿务局南屯煤矿. 用日本 JEM-1200 EX/9100 EDAX 分析电子显微镜对煤矸石中的化学成分进行了能谱分析, 主要化学组成列于表 1 中.

### 1.2 煤矸石中铝、铁的酸浸原理

表 1 煤矸石主要化学组成

组成	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{SiO}_2$	$\text{MgO}$	$\text{CaO}$	其它	合计
含量/%	24.42	3.00	64.62	0.84	3.98	3.14	100

南屯煤矸石属于高岭石结构. 高岭石是由硅氧四面体和铝氧八面体堆积而成的双层网结构, 价键饱和和稳定, 晶格骨架牢固不易分开, 活性很低, 当加热到一定温度时, 高岭石晶体失去层间水变成偏高岭石, 有一定的活化能, 使  $\text{Al}_2\text{O}_3$  具有活性, 铝易于用酸浸出. 当加热温度超过 1000℃ 时, 高岭石转变为莫来石, 莫来石晶形稳定,  $\text{Al}_2\text{O}_3$  便失去活性. 所以煤矸石中铝、铁的酸浸是在煤矸石焙烧到一定程度, 使其中的  $\text{Al}_2\text{O}_3$  具有活性的基础上才能完成.

在一定温度下, 煤矸石中的晶体发生物相变化需要一定的反应时间才能完成, 这是焙烧时间对酸浸取率的影响. 从化学动力学的角度

看, 粒度和温度对  $\text{Al}_2\text{O}_3$  的浸取有很大影响, 颗粒越细, 比表面积越大, 反应越容易进行; 温度越高, 反应速度越快. 另外,  $\text{Al}_2\text{O}_3$  的酸溶反应随着酸用量的增加,  $\text{Al}_2\text{O}_3$  溶出越彻底, 当然还应考虑到产品的成本及产品中的  $\text{Al}_2\text{O}_3$  和  $\text{Fe}_2\text{O}_3$  的含量问题.

### 1.3 PAFC 的制备方法及其工艺流程

用煤矸石制备 PAFC 主要是利用煤矸石中含有的  $\text{Al}_2\text{O}_3$ 、 $\text{Fe}_2\text{O}_3$  (为了提高产品的  $\text{Fe}_2\text{O}_3$  含量, 要外加一定量的铁矿石) 与盐酸反应生成

\* 现为清华大学环境工程系博士生

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$\text{AlCl}_3$  和  $\text{FeCl}_3$ , 然后加一定量的碱调 pH 值可制备出 PAFC 产品。

制备方法: 将煤矸石粉碎、研磨、过筛, 在一定温度下焙烧一定时间, 在常压下, 按一定配比将一定浓度盐酸、煤矸石和一定量的铁矿粉装入带有回流冷凝管的反应器中, 在  $110^\circ\text{C}$  下反应一定时间, 冷却、过滤, 滤液用碳酸钙调 pH 值, 得棕红色产品。

该产品在山东省邹城市环保化工厂工业生产了 2 年多的时间, 产品已应用到煤炭、石油化工、冶金等行业的废水处理中。产品生产工艺流程见图 1。

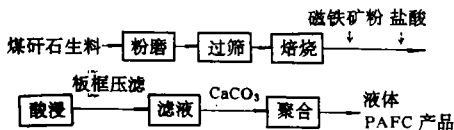


图 1 PAFC 生产工艺流程图

工业 PAFC 产品的比重为 1.30 左右,  $\text{Al}_2\text{O}_3(\%)$  为 5.0 左右,  $\text{Fe}_2\text{O}_3(\%)$  为 3.5 左右, pH 值 2.5 左右。

## 2 PAFC 的结构形态表征

### 2.1 电镜观察

采用 JEM-100 CX II 透射电子显微镜, 将样品滴到有支持膜的铜网上, 用滤纸吸去多余的液体, 晾干后入电镜内观察, 照相。透射电镜观察表明, PAFC 聚合物呈球形, 直径 1.5—8.0 nm 之间。另外, PAFC 产品中混有部分杂质, 可能是  $\text{CaCl}_2 \cdot \text{XH}_2\text{O}$  晶体。

### 2.2 红外光谱分析

采用美国 Nicolet 5 DXFT-IR 仪, 分辨率  $4\text{ cm}^{-1}$ , 扫描频数 60, 用溴化钾作母质压片进行定性测定。PAFC 的红外光谱见图 2。在 PAFC 的红外谱图中, 主要吸收峰的波数为  $3411\text{ cm}^{-1}$ ,  $1631\text{ cm}^{-1}$  强吸收峰,  $1153\text{ cm}^{-1}$ ,  $1104\text{ cm}^{-1}$ ,  $975\text{ cm}^{-1}$ ,  $578\text{ cm}^{-1}$ ,  $468\text{ cm}^{-1}$  处的弱吸收峰。与 PAC 的红外光谱比较 PAFC 与 PAC 在  $3411\text{ cm}^{-1}$ ,  $1631\text{ cm}^{-1}$ ,  $1104\text{ cm}^{-1}$  和  $975\text{ cm}^{-1}$  处有共同的吸收峰, 而  $1153\text{ cm}^{-1}$  处多出一

弱吸收峰。表明在 PAFC 中既有以羟基桥联的铝聚合物, 又有以羟基桥联的铁的聚合物。

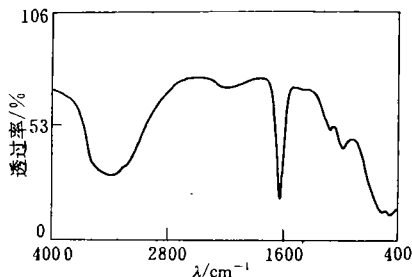


图 2 PAFC 的红外光谱图

### 2.3 X-射线衍射分析

采用日本 D/max-rA 仪, 辐射源为 Cu-K $\alpha$  射线, 电流 50 mA, 电压 40 kV,  $\text{DS/SS}=1^\circ$ ,  $\text{RS}=0.3$ , PAFC 液体样品在  $105^\circ\text{C}$  下进行干燥得固体 PAFC, 固体 PAFC 的 X-射线衍射图见图 3。图 3 表明 PAFC 样品呈现明显的衍射峰, 表明固体有序性好, 可能有多个晶相共存, 在  $10^\circ\text{--}45^\circ 2\theta$  角内出现了多个衍射峰, 可能同时存在拜耳体石(bayerite), 三水铝矿(gibbsite)及水赤铁矿(hydrohematic)等相。

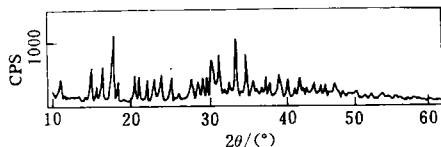


图 3 PAFC 的 X-射线衍射图

## 3 PAFC 在水处理中的应用

### 3.1 用于处理煤矿矿井废水

水样取自兖州矿务局鲍店煤矿, PAFC 的投量为  $40\text{ mg/L}$  (以产品计, 下同), 实验结果见表 2, 结果表明, 仅投加  $40\text{ mg/L}$  的 PAFC, 煤

表 2 PAFC 处理煤矿矿井废水效果

进水/ $\text{mg} \cdot \text{L}^{-1}$		出水/ $\text{mg} \cdot \text{L}^{-1}$		去除率/%	
COD	SS	COD	SS	COD	SS
410.0	1200.0	70.5	120.2	82.8	90.0
495.6	1386.2	89.2	125.3	82.0	91.0
441.8	1218.3	78.1	120.3	82.3	90.1
409.3	1287.3	76.1	129.5	81.4	89.9
435.4	1280.5	76.5	125.1	82.4	90.2

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测定标准偏差的 3 倍计, 方法检测限为  $2 \text{ ng} \cdot \text{ml}^{-1} \text{F}^{-}$ . 对含有  $0.20 \text{ } \mu\text{g} \cdot \text{ml} \text{F}^{-}$  的溶液平行测定了 11 次, 平均回收率为 96.8%; 另外, 加标回收试验表明,  $0.20 \text{ } \mu\text{g} \cdot \text{ml}^{-1} \text{F}^{-}$  的加标回收率为 96%—104%.

2.7 干扰试验

试验了常见共存离子对测定  $\text{F}^{-}$  的干扰情况, 结果表明, 在本文条件下, 大量  $\text{K}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{Cl}^{-}$ ,  $\text{NH}_4^{+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  等对  $\text{F}^{-}$  的测定无干扰; 当  $\text{F}^{-}$  含量为  $0.30 \text{ } \mu\text{g} \cdot \text{ml}^{-1}$  时, 允许 2 倍量的  $\text{Fe}^{3+}$ ,  $\text{VO}_2^{+}$  和  $\text{Cr}_2\text{O}_7^{2-}$  存在, 超过限量时可加抗坏血酸还原消除干扰;  $\text{Al}^{3+}$  的干扰可用蒸馏法去除;  $\text{TiO}^{2+}$ ,  $\text{WO}_4^{2-}$  和  $\text{MO}_4^{2-}$  对测定干扰严重, 但由于多数水样中这些离子的含量很少, 故不致于产生影响. 因此, 本法可望在不经分离的情况下, 直接测定水样中的氟离子.

2.8 样品测定

测定了土壤、蔬菜及不同水样中的氟含量. 样品处理方法如下:  
土壤中可溶性氟: 将  $10.0 \text{ g}$  过筛土样置于  $250 \text{ ml}$  锥形瓶中, 加  $20 \text{ ml}$  蒸馏水后于振荡器上充分振荡浸取  $2.5 \text{ h}$ , 过滤, 滤液稀释至  $50 \text{ ml}$ .  
蔬菜: 将新鲜蔬菜样品用自来水和蒸馏水

反复洗涤数次并去除表面水分后, 称取适量充分搅碎, 加入适量水和  $1.0 \text{ mol} \cdot \text{L}^{-1} \text{HCl}$ , 在充分搅拌下浸取  $2.5 \text{ h}$ , 混合物过滤并将溶液适当稀释后待测.

水样经澄清处理后直接测定.

表 1 样品测定结果/ $\mu\text{g} \cdot \text{ml}^{-1}$

样品	测得量 ( $n=5$ )	加入量	回收率 /%	相对标准偏差 RSD/%
土壤样	3.743 <sup>1)</sup>	1.500	103.2	1.5
番薯叶	8.872 <sup>1)</sup>	1.500	98.1	1.2
海 水	0.440	1.000	98.5	1.7
雨 水	0.075	0.500	102.9	3.5
地表水	0.368	0.500	97.3	2.7

1) 浓度单位为  $\mu\text{g} \cdot \text{g}^{-1}$

用本法测定上述溶液中的氟含量, 并作了加入回收实验, 表 1 中给出了相应的测定结果.

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(上接第 63 页) 矿矿井废水经处理后就可达标排放, 处理  $1 \text{ m}^3$  水的投药费用仅为  $0.04$  元. 目前, 鲍店煤矿对处理后的废水再经适量加药混凝微滤后回用于煤矿生产中.

3.2 用于处理油田含油废水

由于油田废水含油, 机械杂质等, 需经过

净化处理后才能回注地下. 以胜利油田现河首站废水为代表, 考察了 PAFC 用于处理油田含油污水的效果(见表 3), 表 3 表明, PAFC 的投量在  $40 \text{ mg/L}$  以上时, 除油率及 SS 去除率都在 90% 以上, 可满足油田回注水的要求, 这说明 PAFC 是处理油田含油废水的高效净水剂.

表 3 PAFC 处理油田含油废水效果

PAFC 投量 / $\text{mg} \cdot \text{L}^{-1}$	含油量 / $\text{mg} \cdot \text{L}^{-1}$	SS / $\text{mg} \cdot \text{L}^{-1}$	浊度 /度	除油率 /%	SS 去除率 /%
0	140.0	72.4	150	0.0	0.0
20	20.5	15.3	20.6	85.4	79.4
30	15.2	8.4	12.5	89.1	88.7
40	9.1	4.5	8.8	92.5	93.9
50	5.4	2.3	7.7	96.1	96.9
60	4.3	1.8	6.9	96.9	97.6

terephthalic acid (TA) anaerobic degradation. Experiment results indicated that nitrate accelerated sludge growth by denitrification and at the same time, more microorganisms or groups degrading TA were induced and formed. After six-week, the specific TA degradation rate reached 18.75 mg/(gVSS · d) and 10.28 mg/(gVSS · d) respectively by denitrify and methanogenic acclimation. The results also showed that it is possible to transfer TA degradation from denitrification to methane fermentation smoothly within 2—3 weeks.

**Key words:** nitrate, terephthalic acid (TA), acclimation, anaerobic degradation.

**Reclamation Treatment of the Oil Refinery Wastewater Sludges by Sulphuric Acid Catalytic Carbonification.** Yang Runchang and Zhou Shutian (Dept. of Chem. Eng., Xiangtan Univ., 411105); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 54—56

The results from the study showed that the sulphuric acid may allow sludges in the wastewater to carbonize and then separate from the wastewater under the conditions of applied pressure of 0.5—0.7 MPa, temperature of 150—170°C and pH of 1.7—1.8. The granular activated carbon can be produced using the carbon cinder carbonized from wastewater sludges by  $\text{KHCO}_3$  activation. The main quality indices of the product are better than GB/T 13804-92 (China) secondary granular activated carbon. It was found that catalytic carbonification of sludges is lower cost approach of treating wastewater sludges from oil refinery with waste acid.

**Key words:** wastewater sludge, reclamation, activated carbon, oil refinery wastewater treatment.

**Performance of Ultrafine  $\text{Fe}_2\text{O}_3$  for High Temperature Removal of  $\text{H}_2\text{S}$ .** Hou Xianglin et al. (State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 57—58

High temperature removal of  $\text{H}_2\text{S}$  is very important in IGCC process. Using ultrafine particles of  $\text{Fe}_2\text{O}_3$  as  $\text{H}_2\text{S}$  sorbent at high temperature was described in this paper, influences of particle size and temperature were studied, performance of  $\text{Fe}_2\text{O}_3$  particles prepared by supercritical fluid drying was compared with analytical reagent and

$\text{Fe}_2\text{O}_3$  particles prepared by amorphous citrate precursors. Sulfur capacity increased as particle size decreased. Breakthrough time became shorter with increase of temperature. Compared with other metal oxides, sulfur capacity of  $\text{Fe}_2\text{O}_3$  was higher.

**Key words:** ultrafine  $\text{Fe}_2\text{O}_3$ , high temperature desulfurization,  $\text{H}_2\text{S}$  sorbent.

**Preparation of Flocculant PFCS and Study on Its Properties.** Sun Jianhui et al. (Environ. Sci. Institute of Henan Normal University, Xinxiang 453002); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 59—61

New inorganic polymeric flocculant poly sulfuric chloride ferri ferrous (PFCS) has been prepared by using dissolving rolling waste steel residue with mixing acid  $\text{H}_2\text{SO}_4$ -HCl as raw material. The flocculating effect of PFCS has been tested and compared with that of poly sulfuric ferri ferrous (PFS). The experimental results showed that the flocculating effect and removing turbidity are very good in pH range of 6—9. The quantity of PFCS was only 10 mg/L when Yellow River water was treated from 425 turbidity degree to below 5 degree, but the least quantity of PFS was 25 ml/L at the same flocculating conditions. The flocculating effect of PFCS is much better than that of PFS at the same conditions.

**Key words:** poly sulfuric chloride ferri ferrous, flocculant, rolling waste steel residue, resource recovery.

**Study on the Preparation of Polyaluminum Ferric Chloride from Gangue.** Gao Baoyu et al. (Dept. of Environ. Eng., Shandong University, Jinan 250100); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 62—63

Poyaluminum ferric chloride (PAFC), a new type of inorganic flocculant, was prepared by gangue, a kind of waste from coal-mine, and hydrochloric acid as raw materials. The structure of PAFC was studied by transmission electron microscope (TEM), IR spectroscopy and X-ray diffraction. The effect of PAFC in industrial wastewater treatment was tested. The experimental results showed that it is feasible to prepare PAFC from gangue; PAFC produced is the compound of polyaluminum chloride and polyferric chloride. After the wastewaters from coal-mine and oilfield were treated with PAFC in 40 mg/L, the removal ratios of COD, SS and oil are about

08%, 90% and 90% respectively.

**Key words:** gangue, polyaluminum ferric chloride, preparation, structure, wastewater treatment.

**Spectrophotometric Determination of Trace Fluoride Based on the Inhibitory Effect on the Formation of Trinary Complex.** He Ronghuan and Xiu Huanhong (Chemistry Department of Yantai Teachers College, Yantai 264025); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 64–66

A kinetic method for the determination of trace fluoride was established based on the inhibitory effect of fluoride on the formation of trinary complex among Zr (IV), salicyl fluoronol (SAF) and cetyltrimethyl-ammonium bromide (CTMAB). The determination conditions were  $[\text{SAF}] = 6.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{CTMAB}] = 8.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{Zr (IV)}] = 1.0 \mu\text{g} \cdot \text{ml}^{-1}$ ,  $[\text{HCl}] = 0.08 \text{ mol} \cdot \text{L}^{-1}$ ,  $25^\circ\text{C}$ . The calibration graph was linear for  $0.08 - 0.48 \mu\text{g} \cdot \text{ml}^{-1}$ , and the detection limit was  $2 \text{ ng} \cdot \text{ml}^{-1}$ .

**Key words:** inhibitory on trinary complex formation, spectrophotometry, fluoride, determination.

**Gas Chromatographic Determination of Chlorinated Pesticides and Polychlorinated Biphenyls in Sediment Using Ultrasonic Extraction and Steam Distillation Extraction (SDE).** Zou Shichun and Zhang zhanxia et al. (Dept. of Chem, Zhongshan University, Guangzhou 510275); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 67–70

This paper described a new method for the extraction of trace organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) in sediments using a combined technique of ultrasonic extraction (UE) with steam distillation extraction (SDE). The sediment sample was blended with water or n-hexane prior to the SDE step and the high recoveries for DDTs and PCBs, especially for PCBs, could be obtained by an auxiliary UE method. However, the recoveries for BHCs in sediment are unsatisfactory. Further experiments showed that the recoveries for  $\beta$ -,  $\gamma$ -BHC could be enhanced when a small amount of n-hexane was mixed with the sediment sample and was treated with the UE prior to the SDE step. It is possible that this combined technique is used in the extraction for semi-volatile compounds in other solid samples.

**Key words:** steam distillation extraction, ultrasonic bath, organochlorinated pesticides, polychlorinated biphenyls analysis.

**A New PVC-Coated Carbon Rod Electrode for Anionic Surfactants and Its Application in Environmental Monitoring.** Li Congrong (Chengdu Factory of Petroleum Chemistry, Chengdu 610083), Dan Dezhong et al. (Dept. of Environ. Sci. and Eng., Sichuan Union University, Chengdu 610065); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 71–72

A new anionic surfactant selective electrode prepared by coating a graphite rod with PVC compound containing triheptyl-dodecyl ammonium and dodecylbenzene sulfonate THDA-DBS is developed. The optimum coating membrane composition is THDA-DBS 5 mg, DBP 0.4 ml, NB0.3 ml and PVC 0.2 g. The electrode exhibits nernstain response to the surfactant anions over the concentration range  $1 \times 10^{-3}$  to  $8.1 \times 10^{-7} \text{ mol/L}$  with a slope of 58 mV per decade. The detection limits are  $5.6 \times 10^{-7} \text{ mol/L}$  for DBS and  $7.4 \times 10^{-7} \text{ mol/L}$  for SDS. The electrode shows high stability and selectivity, and it is easy to make and store, and inexpensive. The electrode has been used successfully for the determination of anionic detergents in environmental water samples.

**Key words:** ion selective electrode, anionic surfactant, environmental monitoring, water sample.

**Observation on Concentrations of Ammonia in Atmosphere by Diffusive Sampling.** Chen Letian and Tong Yuqin (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(4), 1996, pp. 73–74

Simple passive diffusion samplers were used for the determination of ammonia concentrations in atmosphere. The gas was collected by molecular diffusion on phosphoric-acid-impregnated paper and subsequently determined spectrophotometrically. In a survey of 3 apartments, concentrations of  $\text{NH}_3$  indoors were higher than those outdoors. These preliminary data suggest that humans themselves may be a source of ammonia.

**Key words:** ammonia, diffusive sampling, environmental observation.

**The Strategy, Countermeasures and Cost-Benefit Analysis of Industrial Wastewater Control in**