

含锰废渣吸收低浓度 SO_2 生产 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 研究*

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摘 要 在实验室中进行了含锰废渣吸收低浓度 SO_2 废气生产 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 的研究, 用 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 生产过程中废弃的含锰废渣在玻砂气体吸收器中吸收废气中 SO_2 , 对 SO_2 浓度为 $0.01\text{m}^3/\text{m}^3$ 的废气, 在固液比 $r=1:5$, $\text{pH}=1.8-2.2$, SO_2 吸收效率 $\eta=90\%$ 的条件下生成纯度较高的 MnSO_4 母液, 经简单的除杂、过滤、浓缩、结晶、干燥, 得到 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 含量达到 94% 的产品。

关键词 SO_2 , 含锰废渣, 烟气净化。

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 生产过程产渣中的 Mn 、 Cu 、 Fe 、 Ni 、 Co 、 Mg 、 Al 、 Zn 等, 对 SO_2 水溶液具有催化氧化作用^[1]。据报道^[2], MnO 及 MnO_2 在吸收 SO_2 过程中生成的 Mn^{2+} , 对 SO_2 的氧化具有良好的催化作用, 而在 Fe 、 Cu 、 Al 等金属离子存在的条件下, 由于这些离子的协同效应, Mn^{2+} 离子表现出更强的催化作用^[3]。本研究同时利用 MnSO_2 及 MnO 能直接与 SO_2 反应及生成的 Mn^{2+} 对液相 SO_2 又具有强烈的催化作用 2 个主要特点, 以废渣湿法吸收低浓度 SO_2 , 一步生成浓度较高的 MnSO_4 母液。

1 实验部分

实验装置及流程如图 1 所示。低浓度 SO_2 采用静态配气法配制并贮存在气袋 1 中, 采用浓度约为 $0.01\text{m}^3/\text{m}^3$ 的 SO_2 气体。 SO_2 气体在采样器 8 抽引下, 首先进入盛有锰渣悬浮液的玻砂气体吸收管 3, 吸收后气体再经过装有碘液的尾气吸收管 6, 测定其中 SO_2 的浓度, 原料气浓度由另一吸收管 6 测定, 通过吸收管 6 后的气体由采样器中的转子流量计计量, 整个系统在负压下操作。所用含锰废渣成分见表 1。

表 1 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 生产废渣化学分析结果¹⁾

分析元素	Mn	MnO	MnO ₂	Fe	Cu	Pb	Ni	Co	As	CaO	MgO	Al ₂ O ₃	SiO ₂
含量/%	20.60	12.66	9.51	2.5	0.0025	0.00067	0.018	0.011	0.0067	2.91	0.86	1.82	7.38

1) 渣样取自云南蒙自化工厂渣厂, 布点取样

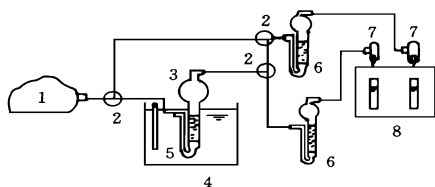


图 1 实验装置及流程

1. SO_2 气袋 2. 三通 3. 吸收瓶 4. 恒温器
5. 温度计 6. 吸收管 7. 缓冲瓶 8. 采样器

由表 1 可知, 含锰废渣中除能直接与 SO_2 反应的 MnO_2 及 MnO 含量各占废渣总量的 9.51% 和 12.66% 外, 其它有利于 SO_2 液相催化氧化的金属离子也占了相当份量。

在实验过程中 Mn 浸出率据 $\text{Mn}\%$ 计算:

$$\eta_{\text{Mn}} = \frac{(\text{Mn}\%)_1 - (\text{Mn}\%)_2}{(\text{Mn}\%)_1} \times 100\% \quad (1)$$

式中, $(\text{Mn}\%)_1$ 为废渣中 Mn 含量; $(\text{Mn}\%)_2$ 为吸收 SO_2 后渣中 Mn 含量。

$\text{Mn}\%$ 分析采用硝酸铵氧化法, SO_2 分析采用碘量法, 吸收浆液体积为 15ml , 用废渣和蒸馏水配制, 吸收液总酸度用标准 NaOH 滴定, 亚硫酸浓度用标准碘液滴定, 所用试剂均为分析纯化学试剂。废渣粒径 $90\% - 100\%$ 目。

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2 实验结果及讨论

2.1 固液比对生成酸浓度的影响

为寻求余酸浓度最小的固液比, 取 10g 废渣配成不同固液比的浆液吸收 SO_2 . 在等吸收率 η 条件下分析母液余酸浓度, 得到各吸收效率 ($\eta=65\%, 90\%, 95\%$) 时固液比对余酸浓度的影响曲线, 其中以 $\eta=65\%$ 时固液比对余酸浓度的影响最大(图 2). 实验结果表明, 吸收效率恒定时, 当固液比 r (质量比) 为 1:30 时余酸浓度最高, $r=1:5$ 时最低, 两者相差 0.1mol/L. 固液比 $r=1:5$ 时, 在 $\eta=65\%$ 下的余酸浓度可达 0.16mol/L. 若 SO_2 吸收效率提高, 余酸浓度还可下降, 故可认为固液比变化引起的余酸浓度变化对以后的中和及除杂过程影响不大.

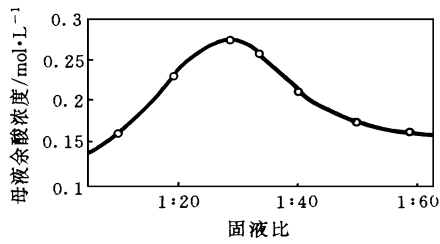


图 2 固液比对母液余酸浓度的影响 ($\eta=65\%$)

2.2 固液对比 SO_2 吸收量影响

考虑到实际应用中 SO_2 吸收效率应 90%, 取 10g 废渣配成不同固液比的浆液吸收 SO_2 , 在等效率 ($\eta=90\%$) 条件下研究固液比对 SO_2 吸收量的影响, 实验结果如图 3 所示.

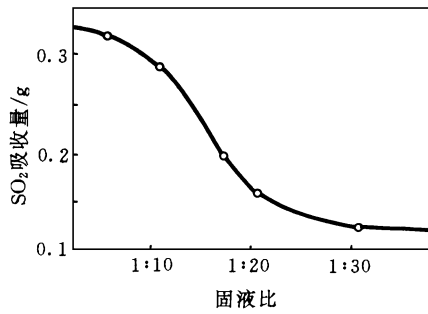


图 3 固液比对 SO_2 吸收量的影响

图 3 表明, 单位废渣吸收的 SO_2 量随固液比增加而增加, 在固液比低于 1:20 时尤为明显, 1g 废渣在不同固液比条件下吸收 SO_2 量可相差 0.2g 左右, 说明固液比对 SO_2 吸收量有明显影响, 从余酸量要小的角度考虑, 固液比以 1:5 为宜, 此时 1g 废渣的 SO_2 吸收量可达 0.3g 左右.

2.3 固液比对 Mn 浸出率影响

在较高的 SO_2 吸收效率下, Mn 浸出率一般较低, 用 10g 废渣在不同固液比条件下吸收 SO_2 , 在等吸收效率条件下 ($\eta=95\%$) 研究废渣中 Mn 的浸出效率受固液比的影响, 实验结果如图 4 所示.

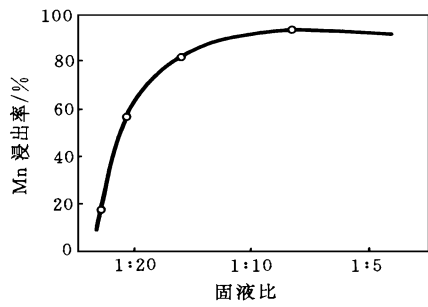


图 4 固液比对 Mn 浸出率的影响

实验结果表明, 随固液比增大, Mn 浸出率增加, 固液比小于 1:10 时尤为明显, 固液比为 1:10 时, 浸出率约为 90%, 固液比大于 1:10 时浸出率可达 92%, 以后趋于平缓。因此, 从 Mn 浸出率的角度考虑, 固液比也宜选 1:5.

2.4 pH 值对 SO_2 吸收效率的影响

为简化操作, 在实际 SO_2 吸收操作中常以 pH 作为吸收操作的主要控制参数, 本文在固液比 $r=1:5$ 时考查了 pH 对 SO_2 吸收率的影响, 以求得 pH 值与 SO_2 吸收率的对应关系, 实验结果如图 5 所示.

图 5 表明, 要控制 SO_2 吸收率大于 90%, 溶液 pH 不能低于 1.8, 在 $\text{pH}=2.2$ 时 SO_2 吸收率明显下降, 当 $\text{pH}=2.2$, 吸收效率可保持大于 98%. 从余酸量和 SO_2 吸收率综合考虑, pH 控制在 1.8—2.2 较为适宜.

废渣中 MnO 湿法吸收低浓度 SO_2 废气生

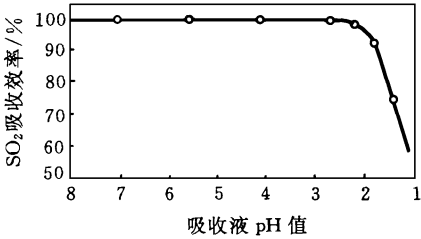
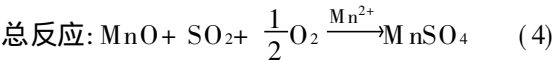
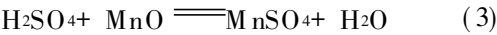
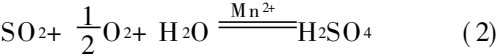
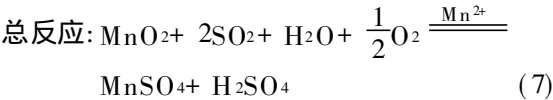
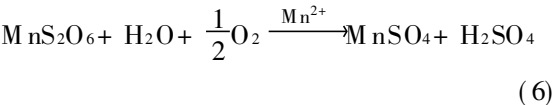


图5 pH 值对 SO₂ 吸收效率的影响

成 MnSO₄ 的反应式如下:



废渣中 MnO₂ 湿法吸收低浓度 SO₂ 废气生成 MnSO₄ 的反应式如下:



反应过程中 Mn²⁺ 的存在对 SO₂ 水溶液的液相催化氧化起到关键作用, SO₂ 的吸收实际上取决于其在水溶液中的催化氧化步骤(2)。本研究将 SO₂ 液相催化氧化吸收与 MnSO₄ 的生产结合起来, 实验一步生成了 MnSO₄ 母液, 工艺简单, 操作控制容易, 母液经浓缩可得 MnSO₄ · H₂O 产品。

2.5 MnSO₄ · H₂O 制取初步研究

在固液比 1 : 5, 吸收终点 pH 为 1.5 条件下, 制取母液操作如下:

一次过滤 中和 加热 静置 二次过滤 浓缩 结晶 产品分析

中和及 pH 调节采用 NaOH, 得到产品如表 2 所示。

表 2 产品含量/%

项目	MnSO ₄ · H ₂ O	Fe	pH	备 注
国标二级	95%	0.008	5—7	GB1622-86 标准
本产品	94.12	1.01	6	按 GB1622-86 检验

与国标二级品相比, 产品 MnSO₄ · H₂O 含量基本达标, Fe 超标较多, 实验过程中母液呈红色, 这是由于 SO₂ 吸收过程中 Fe²⁺ 氧化成 Fe³⁺ 所致, 在 Fe²⁺ 的氧化过程中, MnO₂ 起到了氧化剂作用. 调节 pH 值, Fe³⁺ 在中性条件下可以除去, 产品中总 Fe 含量可降到标准以下^[4]. 本产品 Fe 含量偏高, 一方面是由于废渣中 Fe 相对含量高, 另一方面是由于 Fe²⁺ 不能完全氧化成 Fe³⁺ 所致。

3 结 论

(1) 含锰废渣吸收低浓度 SO₂ 废气生产 MnSO₄ · H₂O 过程中, 固液比对 Mn 浸出率、余酸浓度、SO₂ 吸收容量均有明显影响, 固液比以 1 : 5 较为适宜。

(2) pH 值对 SO₂ 吸收率有明显影响, pH 2.2 时 SO₂ 吸收率 98%, pH 1.8 时 SO₂ 吸收效率急剧下降, pH 控制在 1.8—2.2 为宜。

(3) 在适宜操作条件下, 废渣悬浮液净化吸收低浓度 SO₂ 废气生产 MnSO₄ · H₂O 可一步得到基本合格产品, 该法工艺简单, 易于操作控制. 由于以废治废, 具有明显的环境经济效益, 无论 SO₂ 吸收率及 Mn 回收率均大于 90%。

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spectively. These measurements revealed that SRB can better adapt to conditional changes, and has less attachment ability to granules compared with methanogenic bacteria, which certify the possibility to treat high strength organic wastewater containing sulfate using two phase anaerobic digestion process in microbiological aspects. The effects of sulfate reduction on methanogeneses in anaerobic reactor based on the SRB growth and distribution were discussed.

Keywords: SRB, two phase anaerobic digestion, UASB reactor.

Simulating Toxicity Tests of Methamidophos Pesticide to Soil Animals. Li Zhongwu and Wang Zhenzhong et al. (Dept. of Resource and Environment, Hunan Normal University, Changsha 410081): *Chin. J. Environ. Sci.*, **18** (6), 1997, pp. 45—49

Results of simulating experiments on methamidophos pesticide to soil animals showed that the methamidophos pesticide has an obvious effect on soil animals, the species and the amount of soil animals decrease obviously with increasing of methamidophos pesticide treating concentration; the diversity indexes are 3.7596, 5.7962 and 8.5714 for 0.54ml/L, 0.01ml/L and control of methamidophos pesticide treating concentration respectively. Toxicity test of earthworm showed that the methamidophos pesticide influences obviously earthworm, their LC_{50} are 13.7ml/L, 5.4ml/L and 3.9ml/L for 24 hours, 48 hours and 72 hours respectively. Safe concentration calculated of earthworm living is 0.2517ml/L.

Keywords: soil animal, earthworm, methamidophos, simulating experiment.

Bioaccumulation of Two Speciations of Rare Earth Elements in Rice Seedling. Wang Qin, Sun Hao et al. (State Key Lab of Pollution Control and Resources Reuse, Dept. of Environ. Sci. & Engin., Nanjing Univ., 210093): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 50—52

Bioaccumulation of light, medium, and heavy rare earth elements and their EDTA-complexes by rice seedling was investigated simultaneously. The results showed that the bioaccumulation values in the root and above ground

parts (stem & leave) of the rice seedling were positively correlated with the concentration of the rare earth elements in the culture solution. The results all showed that the ion speciation of the rare earth elements was the effective speciation for the root of plant, the order of bioaccumulation values was: root > stem & leave; the bioaccumulation values of EDTA-complexe in the root decreased obviously, while in the stem & leave the value increased evidently, so the speciation of EDTA-complexe was the effective speciation for the above ground parts of plant.

Keywords: rare earth ion, rare earth-EDTA complexe, bioaccumulation, rice, seedling.

A Study on the Characteristics of Reaction of Dichloramine and Bromide at Water Chlorination. Huang Xuejuan and Zhang Danian (Research Institute of Environ. Eng., East China Univ. of Sci. and Tech., Shanghai 200237): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 53—57

Monochloramine and dichloramine can be formed at water chlorination which containing ammonia. The chloramine react with bromide contained in water. The reaction rate increases with pH elevating and decreases with descent of bromide concentration. There is an introducing period in the reaction, and this period are inverse proportion with logarithm of bromide concentration. The reaction rate is first order reaction for dichloramine. Reaction products are studied by UV spectrum, gas chromatograph and polytetrafluoroethylene micro porous permeation, and Br^- and N_2 have been affirmed. The reaction formula can be inferred.

Keywords: dichloramine water, chlorination, bromide, introducing period, UV spectrum, gas chromatograph, polytetrafluoroethylene micro porous permeation.

Study on SO_2 Absorption with Manganese Waste Slag to Produce $MnSO_4 \cdot H_2O$. Ning Ping et al. (Dept. of Environ. and Che. Eng., Kunming Univ. of Science and Technology, Kunming 650093): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 58—60

The experimental research of SO_2 desulphurization with manganese waste slag from a $MnSO_4 \cdot H_2O$ production plant has been done

in lab.. $0.01\text{m}^3/\text{m}^3$ SO_2 is absorbed in a glass absorber with liquor of manganese waste slag. Under the condition of solid-liquid ratio $\text{SO}_2:1:5$, pH 1.8—2.2 and SO_2 absorption efficiency

90%, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ has been produced by primary crystallization of the absorption mother liquor. The products analysed have a purity of 94% $\text{MnSO}_4 \cdot \text{H}_2\text{O}$.

Keywords: sulfur dioxide, manganese waste slag, wet desulphurization.

Research of Large Gangue Content Cement.

Xu Bin et al. (Dept. of Material Science, Southwest Institute of Technology, Mianyang 621002): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 61—62

By means of activator, a kind of large gangue content cement was obtained, which gangue content is 60% and R_{28} is up to 49.6 MPa. The physical property such as normal consistency water demand, setting time and soundness of cement can meet the standard. The hardened cement has lower porosity of $0.0413\text{cm}^3/\text{g}$ and lower hydrate heat which is 253kJ/kg .

Keywords: large gangue content cement, activator, physical and mechanics property, porosity, hydrate heat.

Study on a Dye Adsorption Made from Waste Asbestos Friction Materials.

Zhao Yuming et al. (State Key Lab of Pollution Control and Resource Reuse, Dept. of Environ. Sci. and Eng., Nanjing Univ., Nanjing, 210093): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 63—65

A kind of new adsorbent was made from waste asbestos friction materials. The static adsorption capacity for cation yellow X-5GL is 159.68mg/g in its aqueous solution which chromaticity is 50000, and the adsorption capacity for cation blue RL is 79.68mg/g in its solution which chromaticity is 5000. The treating amount for waste water generated in the dyeing process from woolen textile factory can be as high as 280ml/g . This adsorbent can also effectively adsorb reactive dye, and can be easily regenerated through aftertreatment when saturated adsorption is reached.

Keywords: asbestos friction materials, adsorption, cation dye, reactive dye.

Study on the Treatment of Skin Wastewater by Sequencing Batch Reactor. Zhu Shuqin et al. (Qiqihar Environ. Protection Sci. Research Institute, and Qiqihar Environ. Supervision Station, Qiqihar 161005): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 66—67

Laboratory studies indicated that experimental conditions: simulating waste water temperature 20°C , DO 2mg/L , COD_Cr 1500mg/L , BOD_5 900mg/L , MLSS 2100mg/L . After 4 hours period aeration, the COD_Cr dropped toward about 100mg/L , BOD_5 toward about 40mg/L , the concentration of sludge increased from 2100mg/L to about 2600mg/L . Experimental results showed that sequencing batch reactor system to be operated in a limit aeration schedule can not cause sludge increase rapidly.

Keywords: sequencing batch reactor, COD_Cr , BOD_5 , MLSS, limit aeration, sludge expansion.

GC Analytical Method for Acidic Phosphate Ester.

Deng Nansheng et al. (Dept. of Environ. Sci., Wuhan Univ., 430072): *Chin. J. Environ. Sci.*, **18**(6), 1997, pp. 68—70

Derivation methods of quaternary ammonium salt thermolysis, silanization, methyl iodide-esterification and diazomethane-esterification for acidic phosphate ester were compared in this paper. Results indicated that methyl iodide-esterification is the best derived method. GC quantitative analysis of this method was systematically studied and a simple, quick, precise and high-sensitivity GC analytical method was developed. Percent recovery of P507 is 97.0%—111% and its detection limit is 0.92ng through this method. Percent recovery of P204 is 94.8%—97.8% and its detection limit is 1.33ng . With the establishing of this method, the studies on the behavior of organophosphorus extracting agents especially the acidic phosphates in water environment reach a new level.

Keywords: organophosphorus extracting agent, acidic phosphate ester, GC, derivation.

Dry and Wet Deposition of Elemental Mercury Measured by Moss Bag near a Mercury Mine.

Tan Hong et al. (Guizhou Research Centre of