

治理技术

硼矿脱除废气中二氧化硫的研究

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摘要 研究硼矿脱硫的工艺条件,提出用低品位硼矿脱除废气中二氧化硫,单塔脱硫率在 80% 以上,硼矿三氧化二硼品位提高一倍。该法经济合理,有利于资源综合利用。

关键词 硼矿脱硫; 二氧化硫废气; 脱硫率。

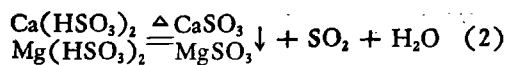
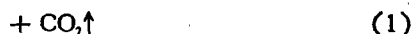
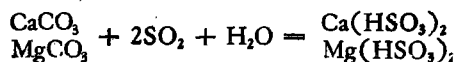
二氧化硫是大气中数量最多,危害面最广的一种气态污染物。长期以来,脱除废气中二氧化硫的研究在国内外一直受到重视。目前,对较高浓度二氧化硫废气,国内外均直接用来生产硫酸或硫磺,而对较低浓度的二氧化硫气体则没有较理想的脱除方法。

脱除废气中二氧化硫的方法很多,硼矿脱硫就是其中一种。我国自八十年代初开始这方面的研究,已取得较大进展。该法不消耗有用的原料,以硼矿中杂质碳酸盐作脱硫剂,二氧化硫脱除率高,吸收后的脱硫剂为硼酸工业原料,是国家急需开发的资源。^[1]

一、实 验

(一) 实验原理

将硼矿粉碎至一定细度,与水按一定比例配制成矿浆,然后通入 SO_2 废气。首先 SO_2 溶于水,生成亚硫酸,再与硼矿中的杂质钙、镁碳酸盐反应,生成亚硫酸氢盐,使硼矿中溶解度小的碳酸盐转化成溶解度较大的亚硫酸氢盐,逸出 CO_2 。 SO_2 吸收后,尾气放空。料浆过滤分离,滤渣即为精硼矿,滤液加热回收 SO_2 ,得副产品亚硫酸盐,滤液循环使用。主要反应如下:



(二) 实验流程

本实验采用泡沫塔单塔吸收,矿浆为连续进料,连续出料,实验流程见图 1。

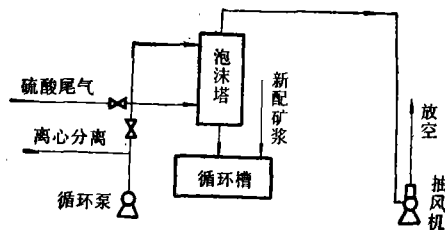


图 1 硼矿脱硫试验流程

(三) 实验条件

1. 脱硫剂 湖南省常宁县硼矿,其化学组成见表 1。

2. SO_2 废气 常宁县化肥厂硫酸车间尾气, SO_2 浓度采用碘量法分析^[2]。每 15min 取样分析泡沫塔进出口 SO_2 浓度一次,实验结果取 8 小时平均值。

3. 废气流量: 120—130m³/h;

4. 液固比 25:1;

5. 液气比 5:1000。

表 1 硼矿主要化学组成*

矿样编号	硼 矿 组 成 (%)					
	B ₂ O ₃	CaO	MgO	CO ₂	SiO ₂	Fe ₂ O ₃
1#	6.49	29.15	21.30	26.47	6.38	5.02
2#	13.37	27.02	25.19	22.00	3.30	1.23
3#	10.45	32.21	21.63	29.17	2.92	1.21

* 硼矿化学组成分析均采用 GB3447-82 硼镁矿石分析方法。

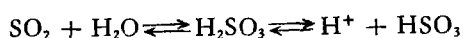
二、结果与讨论

(一) 脱硫率与溶液 pH 值的关系 (见表 2)

表 2 分别表示两种不同品位硼矿的试验结果。由表可知, 脱硫率随溶液 pH 值降低而下降, 因为溶液中存在着如下反应:

表 2 硼矿脱硫率随溶液 pH 值的变化

项 目	溶 液 pH 值					脱硫剂组成 (%)
	6	5	4	3	2	
进塔 SO ₂ 浓度 (%)	0.25	0.25	0.26	0.24	0.32	B ₂ O ₃ = 10.28
出塔 SO ₂ 浓度 (%)	0.015	0.023	0.047	0.061	0.12	CaO = 32.74
脱硫率 (%)	94.0	90.8	81.9	74.6	62.5	MgO = 23.12
进塔 SO ₂ 浓度 (%)	0.32	0.33	0.31	0.31	0.29	B ₂ O ₃ = 6.42
出塔 SO ₂ 浓度 (%)	0.024	0.036	0.049	0.065	0.078	CaO = 28.31
脱硫率 (%)	92.5	89.1	84.2	79.0	73.1	MgO = 21.45



(3)

当溶液中氢离子浓度增加, 即溶液 pH 值降低时, 反应式 (3) 平衡向左移动, 对 SO₂ 脱硫不利, 从而使脱硫率降低。为了保证硫酸尾气处理后达标排放, 应控制溶液 pH 值在 4 以上。

(二) 脱硫率与矿粉细度的关系

硼矿脱硫属液固相反应。矿粉越细, 比表面积越大, 液固两相接触面积也越大, 有利于亚硫酸与硼矿中碳酸盐杂质反应, 从而加速气相中 SO₂ 的溶解, 使脱硫率提高。试验结果见表 3。考虑矿粉动力消耗问题, 一般选用矿粉细度为 95% 通过 100 目即可, 与化肥厂生产配合选择粉碎设备, 便于生产管理。

表 3 矿粉细度对脱硫率的影响

矿粉细度	120 目	100 目	80 目	60 目	40 目
平均脱硫率 (%)	86.4	84.7	80.9	74.8	46.3

(三) 脱硫率、硼矿碳酸盐分解率与溶液 pH 的关系

实验结果由表 4 可知, 硼矿脱硫率随溶液 pH 降低而降低, 而硼矿中 CaO、MgO 的分解率随溶液 pH 值降低而增加, 其中 CaO 分解率增加更显著, 这说明酸度越大, 越有利于碳酸盐分解。由湘硼矿矿物组成可知: 镁硼石含量 11.17%, 硼镁石含量 12.12%, 方解石含量 67.24%。说明硼矿中 CaO 主要以碳酸盐的形式存在, 而 MgO 主要以镁硼石

表 4 脱硫率、硼矿中 CaO、MgO 的分解率与溶液 pH 值的关系

项目	溶 液 pH 值				
	6	5	4	3	2
进塔 SO ₂ 浓度(%)	0.47	0.51	0.45	0.38	0.44
出塔 SO ₂ 浓度(%)	0.038	0.052	0.062	0.085	0.135
脱硫率(%)	91.9	89.8	86.2	77.6	69.3
CaO 分解率(%)	6.2	7.3	23.1	45.7	77.0
MgO 分解率(%)	0.93	1.6	2.2	4.4	6.0

$[\text{Mg}(\text{BO}_2)_2]$ 和硼镁石 $[\text{Mg}_2\text{B}_2\text{O}_4(\text{OH})_2]$ 的形式存在.

(四) 脱硫与硼矿综合利用的关系

以硼矿作脱硫剂处理 SO_2 废气后, 所得

精矿的组成见表 5。由表 5 可知, 脱硫后的硼矿即为精矿, 其中 B_2O_3 含量成倍增加, 矿中有害杂质 CaO 含量大大减少, 该精矿是生产硼酸的好原料。

表 5 脱硫后的精矿主要组成(%)

矿样	1#		2#	
主 要 组 成	B ₂ O ₃	CaO	B ₂ O ₃	CaO
原 硼 矿	6.43	29.91	10.28	32.74
精 硼 矿	10—14	7—12	18—24	6—17

我国硼矿资源丰富,但低品位硼矿多,氧化钙含量很高,至今未能开发利用。现在我国大量开采和利用的仍是硼镁矿。经过多年的开采,硼镁矿已出现了逐渐贫化和后备矿源不足等问题,为了稳定硼系化合物生产,必须研究低品位硼矿资源的利用技术,以求达到工业化应用的可能性。因此,利用废气

SO₂ 来处理硼矿,而硼矿又作为脱硫剂参加反应,通过该化学法选矿,达到硼矿富集的目的,废气SO₂污染又得到了治理,“以贫治废”,一举两得。现以化肥厂为例,将硼矿脱硫资源综合利用关系示于图2。

三、结 论

1. 本法在保证硼矿脱硫剂脱硫后, 硼矿三氧化二硼品位提高一倍以上, 所得精矿可用于硼酸生产; 单塔脱硫率大于 80%。

2. 本法原料较丰富, 资源利用合理。对环境保护和硼矿的开发利用具有现实意义。

参考文献

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(收稿日期 1990 年 2 月 20 日)

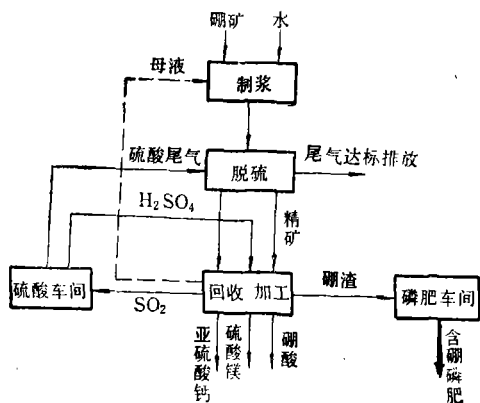


图2 化肥厂硼矿资源综合利用示意图

in. J. Environ. Sci., 12(1), 1991, pp. 47—49

Presented in this paper is the technological conditions of desulfurization in waste gas by using boric ore. Sulfur dioxide in the gas was removed by low-graded boric ore with a desulfurization rate of over 80% in single tower, and the grade of boron trioxide in the boric ore was improved one-fold. This method seems to be favourable to harness the waste economically and to utilize natural resource rationally.

Key Words: desulfurization, waste gas, boric ore.

Purification of Benzene-Containing Exhaust by Using A Tubular Membrane Separator.

Yao Shu, Zheng Lian-ying, Liu Mo-e (Department of Chemical Engineering, Zhejiang University, Hangzhou): *Chin. J. Environ. Sci.*, 12(1), 1991, pp. 50—54

In order to explore purification of benzene-containing waste gas from some industries such as motorcar and machine manufacture, a two-step method is presented in this paper. Because of large volume and low concentration of benzene content, the gas had firstly to be concentrated. In the process, the membrane separation technique was used to concentrate it into high-concentrated and small-volume benzene steam, and then was treated with catalyst combustion or retrieved. A tubular separator made of silicone rubber was used to remove benzenes from waste gases in the experiments. The separate factor and Reynold's number of the gases flowing through the membrane separator were correlated. The results offer a useful tentative idea for further scale-up design.

Key Words: purification of benzene-containing exhaust, tubular membrane separator, silicone rubber.

Treatment of the Effluent Containing High-Concentrated Phenolic Aldehyde by PVA Fibre.

Yan Qiu-lan (Changchun Institute of Geography, Academia Sinica, Jinin); Wu Dun-hu (Dalian College of Railway, Liaonin): *Chin. J. Environ. Sci.*, 12(1), 1991, pp. 54—58

In order to study the adsorption efficiency of PVA fibre and its affecting factors during treating the effluent of high-concentrated phenolic aldehyde, the threshold of adsorption capacity of the fibre, pH of the effluent and duration of the fibre soaked in it were investigated. The experimental results showed that the effect of phenol removal with PVA fibre was apparent, removal rate was above 98%, but the effect of aldehyde removal was not so obvious. The reproduction of PVA fibre, its life-span and treating the wastewater once again with it were also discussed. The efficiency of alkali-washing PVA fibre was above 99%, and its adsorption capacity didnot change by

61 tests. After twice adsorption of the effluent, phenol concentration of outlet water was 0.3 mg/L, lower than the discharge standard provided by the State.

Key Words: treatment of effluent, high-concentrated phenolic aldehyde, PVA fibre.

A Glassy Carbon Electrode Modified Electrochemically with Anthranilic Acid and Its Application to Determination of Lead.

Xu Jin-rui, Zhuang Xiu-run (Department of Applied Chemistry, Huachao University, Quanzhou, Fujian): *Chin. J. Environ. Sci.*, 12(1), 1991, pp. 59—62

Reported in this paper is a method for preparation of a glassy carbon electrode modified with anthranilic acid electrochemically. The modification was carried out in a 50 ml of aqueous solution containing 0.3g anthranilic acid, 0.3g formaldehyde and 0.3g NaOH, by sweeping the glassy carbon electrode potential between -0.1 and +1.3 V (vs.SCE) with scan rate of 100 mV/s for 5 min under stirring. The behaviour of lead on this electrode was also investigated by anodic stripping voltammetry. The redox process of the lead on this modified electrode was irreversible. The sensitivity of this electrode for lead was much higher than that of unmodified one. The modified electrode showed excellent reproducibility with a relative standard deviation of ca. 1.8%(n=12). It was applied to determination of trace lead(II) in water and the optimal conditions were 0.05mol/L KCl (pH= 2—8) as supporting electrolyte, -0.9V (vs.SCE) and 2 min for pre-electrolysis. The determination of lead didnot be interfered by common ions, and obtained a 96—102% recovery for 1—3 ng/ml of lead(II). The lower limit of the quantitative determination of lead was 0.2 ng/ml.

Key Words: glassy carbon electrode, anthranilic acid modification, determination of trace lead.

Analysis of Trace Organics in Soaking Water at the Simulated Water Tanks Using GC/MS.

Kang Jun-xing, Zhao Li-wen (Beijing Municipal Center for Hygiene and Epidemic Control); Zhao Guo-dong, Wei Ai-xue (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, 12(1), 1991, pp. 62—68

Trace organics in soaking water at the simulated water tanks coated with a rustproof paint, 6201 epoxy resin and HJ-polyurethane respectively, were preconcentrated by using mixed resins prior to analysis by column GC/MS. More than one hundred organics have been identified, and the data obtained are available for assessment of water tank material and its effect on water quality.

Key Words: GC/MS Analysis, trace organics, soaking water in water tank.