

双极性膜电渗析法在脱硫废液 NaHSO_3 再生过程中的应用研究*

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摘要 介绍了用双极性膜电渗析法对烟气脱硫废液(NaHSO_3)进行再生的方法. 使用自制均相双极性膜和上海产异相双极性膜, 配以均相阳离子交换膜, 均能以满意的转化率(80%以上)实现再生. 再生过程中电流效率的下降(由 80%左右下降到 20%左右)是由于酸室中氢离子浓度升高所致. 脱硫废液中少量硫酸钠的存在对再生过程无明显影响. 目前阻碍该法实际应用的主要问题是国内试制膜的寿命较短.

关键词 双极性膜电渗析, 烟气脱硫, NaHSO_3 再生.

烟气中 SO_2 脱除的技术方法主要有吸收法、吸附法和氧化法等几类^[1]. 应用较多的是吸收法, 其中已用于工业的湿式吸收法有氨法、钠法、双碱法、镁法和碱性硫酸铝法等. 钠法中的威尔曼-洛德法(亚硫酸钠循环吸收法)是国外用于烟气脱硫最普遍的方法之一. 本工作采用双极性膜电渗析法实现了 NaHSO_3 向 Na_2SO_3 的转化^[2, 3].

1 实验装置与实验方法

实验装置的流程如图 1 所示, 其主要设备是双极性膜电渗析器. 它是多层并联的板框式设备, 由双极性膜和阳膜分隔成碱室与酸室(即两室模型), 整个电渗析器由 4 对碱室与酸室并联构成, 器的两端分别为阳极室与阴极室. NaHSO_3 溶液(相当于脱硫废液)按一定的量比分别加入酸室罐 2 与碱室罐 4. 用酸室泵将溶液送入酸室, 在酸室与酸室罐构成的系统中循环, 在此过程中溶液中的 NaHSO_3 与双极性膜分离出来的 H^+ 作用, 生成 H_2SO_3 , 以 SO_2 的形式放出, 同时 Na^+ 透过阳膜进入碱室. 用碱室泵 5 将溶液送入碱室, 并在碱室与碱室罐构成的系统中循环, 在此过程中 NaHSO_3 与双极性膜分离出来的 OH^- 和酸室来的 Na^+ 作用, 生成 Na_2SO_3

(图 2), 使溶液再生, 可重新用于吸收 SO_2 .

实验中所用均相双极性膜为本实验室用聚砜作基材分别经碘化、氯甲基化和胺化而制得, 异相双极性膜为上海化工厂用阴、阳离子交换树脂和聚乙烯压合制成. 异相阳膜为上海化工厂产 3361 聚乙烯异相阳离子交换膜, 均相阳膜是上海原子核研究所产的以聚乙烯为基膜经辐射接枝制成的均相离子交换膜. 本实验中主要使用了均相双极性膜与聚乙烯基均相阳膜和异

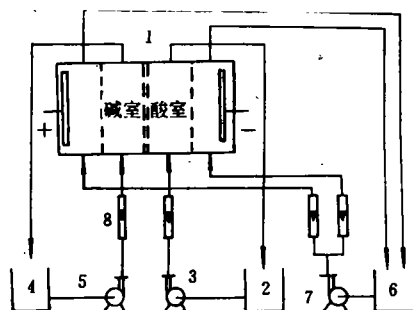
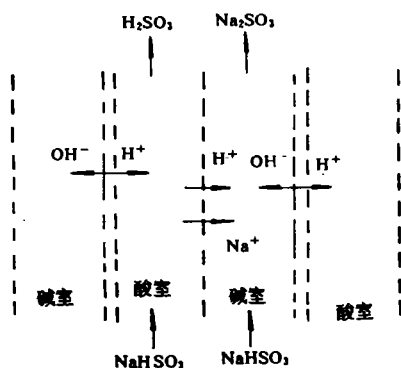


图 1 实验装置流程图

1. 电渗析器(其中===表示双极性膜; ---表示阳膜)
2. 酸室罐 3. 酸室泵 4. 碱室罐 5. 碱室泵
6. 极室罐 7. 极室泵 8. 流量计

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图2 NaHSO_3 再生原理示意图

== 双极性膜; --- 阳膜

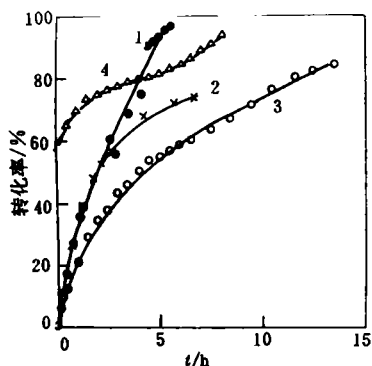
相双极性膜与异相阳膜 2 种组合。

实验在不同的固定电压下进行, 通过测定电流、测定碱室与酸室中循环液的 pH 值变化求知 NaHSO_3 转化的程度和转化量, 根据 NaHSO_3 的转化量与电流可推算过程的电流效率。转化过程的主要工艺技术指标是转化率、转化的电流效率、通过膜的电流密度、能耗及膜的稳定性、寿命和价格。

2 实验结果与讨论

2.1 转化率

图 3 是用膜组合 I 和膜组合 II 对不同起始浓度和含量的 NaHSO_3 溶液进行的再生实验结

图3 NaHSO_3 的转化率与时间的关系

1. 膜组合 I (碱室起始液为纯的 NaHSO_3 溶液, 浓度 1 mol/L)
2. 膜组合 I (碱室起始液为纯的 NaHSO_3 溶液, 浓度 15% (W/W))
3. 膜组合 II (碱室起始液为纯的 NaHSO_3 溶液, 浓度 1 mol/L)
4. 膜组合 II (碱室起始液为 NaHSO_3 和 Na_2SO_3 溶液, 浓度各 0.5 mol/L)

果。由图 3 可知, 使用 2 种膜组合均能获得满意的转化率。其中, 用膜组合 I (自制的聚砜型均相双极性膜和均相阳膜的组合), 效果尤为显著, 以达到 80% 转化率 (从纯 NaHSO_3 开始) 所需时间计, 组合 I 比组合 II 要节省 3/4 的时间。由此, 一方面可说明转化的可行性, 另一方面也可说明自制膜的优越性。

2.2 电流与电流效率

无论使用哪种双极性膜, 在操作的初始阶段, 随着电渗析过程的进行, 通过膜的电流 (及电流密度) 都会逐渐降低 (见图 4)。这一点在自制膜上反映得更突出。电流降低是由于双极性膜电阻增大所致。可能的原因是: 在电渗析过程进行时, 双极性膜中水分被不断电离成 H^+ 和 OH^- 而移去, 从而造成阴、阳膜界面处水含量下降, 而从膜外向膜内补充水分的速度是有限的。补充速度一旦跟不上分解速度, 就会造成电阻的上升和电流的下降。由于自制膜为致密膜, 相对于异相膜来讲水分补充更难一些, 故而电流下降更快。

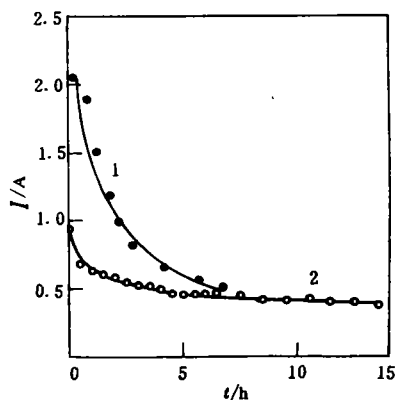


图4 电流随时间的变化

1. 膜组合 I (碱室起始液为纯的 NaHSO_3 溶液, 浓度 1 mol/L)
2. 膜组合 II (碱室起始液为纯的 NaHSO_3 溶液, 浓度 1 mol/L)

电流效率亦随着过程的进行而下降 (见图 5)。这是因为, 随着 NaHSO_3 转化率的上升, 酸室中 H^+ 浓度不断提高, 而 Na^+ 浓度不断降低, 因此, 透过阳膜进入碱室的 Na^+ 与 H^+ 比例逐渐变小。由于进入碱室的 H^+ 和产生的 OH^- 结合又重新生成水, 抵消了双极性膜离解水的作用,

因此使得电流效率下降。

异相膜组合比均相膜组合的电流效率低的原因可能还由于异相膜孔隙率较大、孔径较大,致使酸室中产生的 SO_2 扩散到碱室所致。

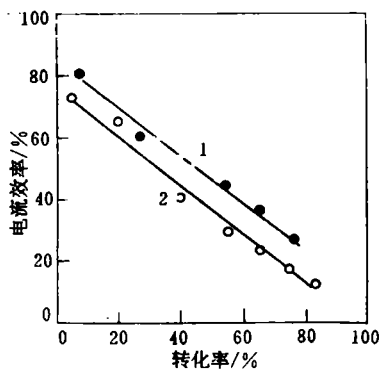


图 5 电流效率与转化率的关系

图注同图 4

2.3 脱硫液中 Na_2SO_4 对过程的影响

由于 SO_3^{2-} 比较容易被氧化,所以脱硫液中总会含有少量 Na_2SO_4 。为了实验验证 Na_2SO_4 的存在对过程的影响,特加大溶液中 Na_2SO_4 的含量以突出其作用。实验结果表明, Na_2SO_4 的存在对过程无不利影响。相反,由于 Na_2SO_4 的存在,酸室中 Na^+ 浓度还会有所增加,结果使电流效率略有上升,有助于过程快速实现(图

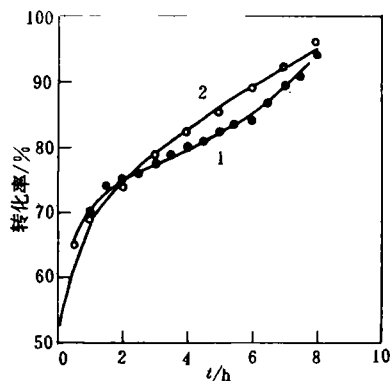


图 6 Na_2SO_4 对过程的影响

膜组合 I, 碱室起始液一定

1. 酸室起始液浓度 1 mol/L NaHSO_3

2. 酸室起始液为 $\text{NaHSO}_3 + \text{Na}_2\text{SO}_4$ 各 0.5 mol/L

6). 可以推断,少量 Na_2SO_4 的存在应该对过程无大影响。

2.4 膜的耐久性实验

从图 7 可见,在膜使用了 100 h 之后,性能便有所下降,这也是目前膜的主要缺陷所在。

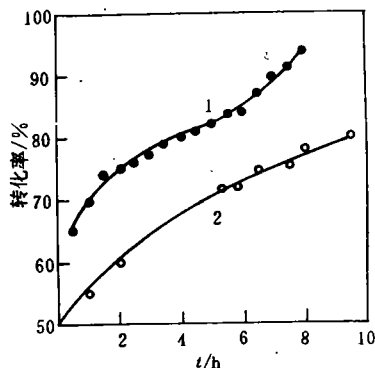


图 7 膜的耐久性实验结果

膜组合 I, 酸、碱室起始液浓度一定

1. 初次实验结果 2. 100 h 之后的实验结果

3 结论

用双极性膜电渗析法可以实现脱硫废液的再生。使用自制均相双极性膜和上海产异相双极性膜都能以满意的转化率使 NaHSO_3 再生为 Na_2SO_3 。但欲使该技术最终得以在生产上实现,下面 2 个问题需要进一步研究解决。① 膜的稳定性差。这应该从改善制膜工艺和选择更佳膜材料入手加以解决;② 转化率高时电流效率低。分析其原因可能主要是酸室中 SO_2 浓度增高所致,因此可在过程和装置设计时设法使酸室中所产生的 SO_2 得以及时除去。

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creasing with reaction time under conditions of 0.85 MPa and 900°C, and the conversion rate is in range of 23.5% to 42% at 120 minutes. The conversion rate is drastically growing with temperature under conditions of 1.15 MPa and 750–950°C at 120 minutes. The conversion rate was slowly and linearly increasing with pressure under condition of 860°C. Finally, the reaction mechanism was discussed.

Key words: pressurized thermogravimetric analysis, limestone, dolomite, desulfurization.

Study on the Regeneration of NaHSO_3 in the Recovery of SO_2 from Flue Gas by Bipolar Membrane Electrodialysis. Yu Lixin et al. (Department of Chemical Engineering, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 40–42

Bipolar membrane electrodialysis is adopted in the regeneration of NaHSO_3 , which is used as absorbent of SO_2 from flue gas. When cation-exchange membrane is supplemented with , both homogeneous and heterogeneous bipolar membranes which are made in our lab and by Shanghai Chemical Factory, respectively, can produce satisfactory conversion ratio (higher than 80%) in the regeneration process. The decrease of current efficiency (from approximately 80% to approximately 20%) is resulted from the increase of the concentration of proton in acid chamber. The existence of small amount of Na_2SO_4 in NaHSO_3 solution doesn't cause much effect on regeneration process. The short membrane lifetime hinders the process from getting into practical application.

Key words: bipolar membrane electrodialysis, recovery of SO_2 from flue gas, regeneration of NaHSO_3 .

Study on Characterization of Adsorption of Zinc onto five types of soil in Beijing Area. Zhou Wei and Li Jiyun (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 43–45

The results of study on adsorption of zinc onto five types of soil in Beijing area showed that the capacity of five types of soil adsorbing zinc presents positive correlation with pH value of the soil solution, contents of organism and CaCO_3 etc in soil. The adsorption data could be fitted to the Freundlich-type equation.

Key words: adsorption, zinc, soil, Beijing area.

A Study on Acclimation Technique of Activated sludge and Biological Treatment of High Consistence Cheni-thermomechanical Pulp Wastewater. Chen Min (Guangdong University of Technology, Environment & Resource Engineering Department, Guangzhou, 510090), Sung-Nien Lo and H-Claude Lavallée (Université du Québec à Trois-Rivières, Québec, Canada, G9A 5H7); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 46–49

The treatment of high consistence Cheni-thermomechanical Pulp (CTMP) pulping wastewater using activated sludge method was studied in this paper. The effect of improving technique in activated sludge acclimation on the sludge settleability and removal efficiencies was discussed. The Experiments showed that the improved technique i. e

combination of batch and continous feed in sludge acclimation process can remarkably improve the sludge settleability and removal efficiencies. The sludge volume after 30 minutes of settling was 290–320 ml/L, sludge volume index was 48–55 ml/g, the removal of COD reached to 77%–85%, removal of BOD_5 was 90%–95%, removal of TSS was 75%–89%.

Key words: batch feed, continous feed, activated sludge, acclimation technique, CTMP wastewater.

Test of Tar Emulsified Liquid as Dust Suppressant for Dirt Roads. Wu Chao et al. (Dept. of Resources Exploitation Engineering, Central South University of Technology, Changsha 410083); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 50–52

In order to control the dust raising on the dirt roads efficiently, the tar emulsified liquid with low concentration was taken as the dust suppressant. Based on a great number of experiments in laboratory, the optimum compositions of surfactants and the prepared condition for emulsifying tar were achieved, tar is 3%–6%, surfactants is 0.5% and water is 93.5%–96.5 Wt. %. The prepared temperature is greater than 70°C. Depended on a lot of tests both in laboratory and field, the results showed that the liquid is very efficient for binding dust and maintaining the dirt roads. The active time can reach more than 10 days, when the liquid is sprinkled on the road in 2.2 kg/m². A rational profit can also be achieved after it is used for years.

Key words: dust suppressant for roadway, tar emulsified liquid, field test.

Electrochemical Separation Process for Recovery of Gold, Silver and Lead from Scrap. Liang Huqi et al. (Dept. of Chem. Eng., Shanghai University, 200072); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 53–56

The electrochemical separation process for comprehensive recovery of gold, silver and lead from Au, Ag-containing scrap was investigated. The smooth and dense cathodic deposit with purity of 99% Pb was prepared by electrochemical separation process under the optimum technological conditions (electrolyte composition: 70 g/L Pb^{2+} , 100 g/L total SiF_6^{2-} ; solution temperature: 40°C. current density: 100 A/m²; concentration of β -naphthol to bone glue: 0.002 g/L and 0.5 g/L) experimentally. The current efficiency of lead was higher than 98%, the specific electric energy consumption was 117 kW · h/tPb. The recovery of Au and Ag in the anode slime were as high as 99% and 98% respectively.

Key words: recovery of Au and Ag, electrochemical separation, treatment of scrap.

Effects of Low pH Value and Aluminum on Uptake of ^{45}Ca by *Misgurnus anguillicaudatus*. Kong Fanxiang et al. (Dept. of Environ. Sci. and Eng., Nanjing University, Nanjing 210093); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 57–59

The effects of low pH value and with or without the addition of aluminum on the uptake of ^{45}Ca by *Misgurnus anguillicaudatus* were studied. The results showed that