Regenerating Flue-Gas Desulfurizing Agents by Bipolar Membrane Electrodialysis

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An experimental study was carried out on the regeneration of a flue-gas desulfurizing agent by using bipolar membrane electrodialysis (BMED) with sodium sulfate (Na_2SO_4) as the supporting and rinsing electrolyte, and piperazine sulfate ($Pz{\cdot}H_2SO_4$) as a model compound for the heat stable salt formed in the process of desulfurizing. The results indicate that the low energy consumption and high current efficiency are achieved when applying electrolyte solutions with a concentration range about 0.3~0.4 mol/L, piperazine sulfate solution with a concentration range about 0.08~0.13 mol/L, and BMED stack of BP-C-C configuration. The results also indicate that when applying a high current density to the BMED stack, it has a high current efficiency and energy consumption. The process cost is estimated to be \$0.96/kg Pz for the regeneration of piperazine with the laboratory-scale experimental equipment, indicating that the process is not only scientifically novel but also economically feasible and attractive besides its potential environmental benefits.© 2005 American Institute of Chemical Engineers *AIChE J,* 52: 393–401, 2006
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Introduction

Sulfur oxides, which can cause acid rain and air pollution, are produced primarily in the process of combustion of fossil fuels, smelting of ores containing sulfur, and production of sulfuric acid and sulfates.[1] As one of the major air pollutants, sulfur dioxide (SO_2) has been under increasingly stringent control on the world scale. In order to obtain the sustainability of development, scientists have to take into consideration the conversation, recycling, and substitution of resources when carrying out pollution control. Up until now, many categories of flue-gas desulfurizing methods have been developed. Some of these categories are wet sorption, dry sorption, catalytic oxidation,[2] electrochemical membrane conversion,[3,4] and RF-plasma conversion.[5] In comparison with other flue-gas desulfurization processes, wet sorption processes are preferentially applied. Furthermore, some kinds of amines are widely used as desulfurizing agents because they are effective and convenient. However, in the process of removing SO_2 from the flue-gas by using an amine solution, heat stable salts are formed and cause a secondary pollution and/or waste of resources.

Piperazine (Pz) is known as a commonly used modifier to remove carbon dioxide from synthesis gas.[6-9] In fact, it is also an ideal desulfurizing agent for flue gas because of the fast kinetics of the sorption reaction, and the property for the formed piperazine sulfite ($PzH_2^{2+}SO_3^{2-}$ or $[PzH^+SO_3^{2-}]^-$) to be regenerated by heating. However, more and more piperazine sulfate ($PzH_2^{2+}SO_4^{2-}$ or $[PzH^+SO_4^{2-}]^-$) will be formed in the circulation because of the oxidation of sulfur dioxide and/or piperazine sulfite, and it cannot be thermally regenerated. The

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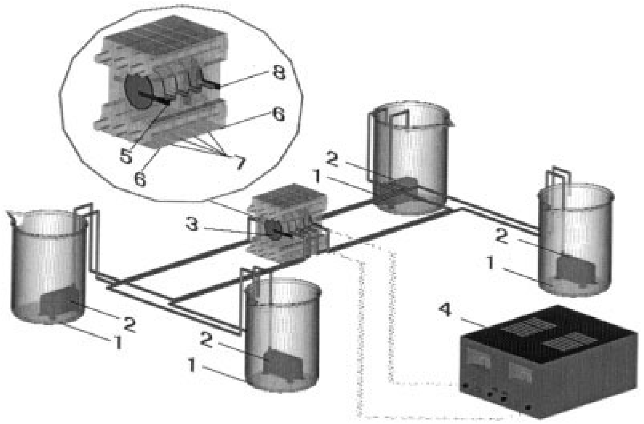


Figure 1. Experimental equipment for regenerating piperazine by using BMED.

(1) Beaker, (2) immersible pump, (3) BMED stack, (4) direct current power supply, (5) cathode, (6) polar plate, (7) compartment spacer, (8) anode.

heat stable salt not only decreases the efficiency of desulfurizing operations, but also causes a secondary pollution and waste of resources.

Bipolar Membranes Electrodialysis (BMED) has been drawing more and more attention from all over the world for its effective functional integration of the electrical field-enhanced water dissociation of bipolar membranes[10-15] and the salt dissociation of conventional electrodialysis. Because of the resulting preponderance in cost and the capability of protecting the environment from secondary pollution, it has already had some successful applications in the chemical industry, food processing, and environmental protection in the last decade.[16,17] Applying BMED to the treatment of stained desulfurizing agents can not only regenerate the agent and keep the circulation steady and stable for a much longer time, but also achieve the recycling of resources.

Therefore, in this article, an experimental study was carried out on the regeneration of a flue-gas desulfurizing agent by using BMED with sodium sulfate as the supporting and rinsing electrolyte, and piperazine sulfate as a model compound for the heat stable salt formed in the process of desulfurizing. The experimental data will lay a foundation for further application in the industrial waste solution discharged in the process of desulfurizing.

Experimental

Sample preparation

Piperazine sulfate ($Pz{\cdot}H_2SO_4$) wasn't commercially available, so it was prepared by the following procedures: (1) Purify the commercially available piperazine ($Pz{\cdot}6H_2O$) according to the method described in literature[18]; (2) Add a solution of sulfuric acid to a solution of piperazine in an excessive amount; (3) Evaporate some water out of the solution and crystallize the piperazine sulfate at 4°C; (4) Wash the crystal with cold distilled water and dry it overnight at 105°C.

Apparatus

As shown in Figure 1, the laboratory-scale experimental equipment is mainly comprised of four parts: (1) the direct current power supply (DF1731SD2A, Zhongce Electronics Co. Ltd., China) used to provide the BMED system with a direct and constant current field; (2) beakers; (3) immersible pumps (AP1000, Zhongshan Zhenghua Electronics Co. Ltd, China) to circulate the solutions at the maximal speed of 27 L/h; and (4) BMED stack. There were four configurations used in these experiments to regenerate piperazine by using BMED, as shown in Figure 2. What is in common among the four stacks are the cathode and anode, which are both made of titanium coated with ruthenium; the Plexiglas spacers (thickness = 9 mm) to keep the membranes apart, with Viton gaskets as the seals; the bipolar membrane (Neosepta BP-1 from Tokuyama, Japan, Table 1) with an effective membrane area of 7.07 cm^2; and the supporting electrolyte solution and electrode rinsing solution, which were both prepared from sodium sulfate (Na_2SO_4). What is different is that a certain number of cation-selective membranes (FT-FKB from FumaTech Germany, Table 1) and/or anion-selective membranes (FT-FAB from FumaTech, Germany, Table 1) were chosen to make up the systems corresponding to different configurations. The BP-C-A configuration (Type I) was applied to all the experimental runs except the ones designed for configuration effect. The four corresponding compartments are: cathode compartment, base compartment, salt compartment, and anode compartment.

All the experiments were undertaken at a certain constant current strength, and the voltage drop across the stack was measured with a digital multimeter (GDM8145, Good Will Instrument Co. Ltd., Taiwan). Before a current was applied, the independent solutions were circulated for a certain amount of time until the voltage drop across the stack was less than 0.2 V, and all the visible gas bubbles in every compartment were eliminated. The concentration of the piperazine formed was determined by using UV-spectrophotometry. The pH values were measured with a pH meter (PHS-3C, Shanghai Leici Instrument Co. Ltd., China).

Calculation of current efficiency and energy consumption

The current efficiency η was calculated as Eq. 1[16]

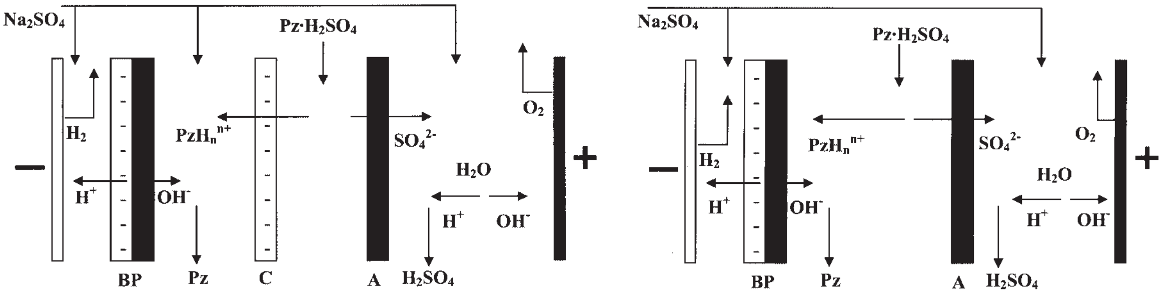
$$\eta = \frac{2(C_t - C_0)VF}{It} \tag{1}$$

where C_0 and C_t are the concentration of piperazine at time 0 and t, respectively. V is the circulated volume of solution in the base cycle, I the current, and F the Faraday constant. Because two Faraday electricity was consumed to form one mole piperazine (see Eq. 2), there exists a coefficient "2." In this work, t was equal to 1 h, and the change of fluid volume in each cycle was negligible, that is, $V = 0.5$ L

$$\mathrm{PzH}_2^{2+} + 2OH^- \Leftrightarrow Pz + 2\mathrm{H_2O} \tag{2}$$

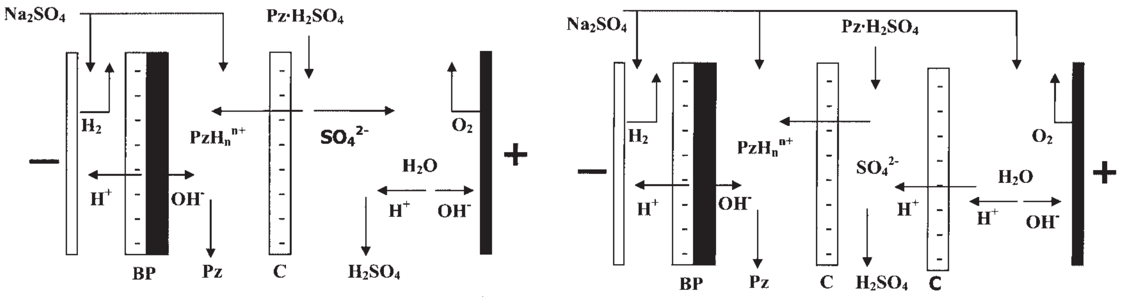
The energy consumption E (kW•h/kg) was calculated by extrapolating the results for the production of 1 kg of piperazine based on Eq. 3[16]

$$E = \int \frac{UIdt}{C_t VM} \tag{3}$$



(a) BP-C-A configuration (Type I)

(c) BP-A configuration (Type III)



(b) BP-C configuration (Type II)

(d) BP-C –C configuration (Type IV)

Figure 2. The BMED stacks of different configurations.

(BP) Bipolar membrane, (C) cation-selective membrane, (A) anion-selective membrane.
(a) BP-C-A configuration (Type I), (b) BP-C configuration (Type II), (c) BP-A configuration (Type III), (d) BP-C-C configuration (Type IV).

where *U* is the voltage drop across the BMED stack (V), and *M* the molar weight of piperazine (86.14 g/mol).

All the experimental data were determined through three independent measurements, and the uncertainty with those results was estimated to be approximately ± 5%.

Results and Discussion

Effect of electrolyte concentration on piperazine regeneration

As described in the Experimental section, the BP-C-A configuration (Type I) was applied to all the experimental runs except the ones designed for configuration effect hereinafter. Figure 3a demonstrates the change of piperazine yield with electrolyte concentration. It can be observed that piperazine yield has not been affected significantly by electrolyte concentration except an increase with time elapse.

Figure 3b shows the effect of electrolyte concentration on the voltage drop across the stack. The results indicate that the higher the electrolyte concentration is, the lower the voltage drop will be. When it comes to the sharp increase of the voltage drop shortly after a current is applied, there are two major reasons for why that happens. For one thing, water dissociation occurs in the interface region of the bipolar membrane after the electrolyte is depleted, which leads to a sharp increase of the bipolar membrane resistance.[19] For another, the H_2 and O_2 generated in the electrode reactions occupy some volume of the two electrode compartments, which leads to a decrease in the apparent conductivity of the electrode rinsing solutions. The conductivity of piperazine (Pz) is much lower than piperazine sulfate ($Pz{\cdot}H_2SO_4$), so the electrical resistance of the stack increases when piperazine sulfate is converted to piperazine, which becomes apparent only in the back part of the voltage drop-time curve when there is much less piperazine sulfate left.

Figure 3c shows the effect of electrolyte concentration on energy consumption and current efficiency. As the electrolyte concentration increases, the energy consumption decreases because electrolytes can reduce the electrical resistance of the stack. However, the electrical resistance of the electrolyte solutions accounts for a much smaller proportion in the total resistance as the concentration increases, and thus the energy consumption decreases in a much smaller magnitude. As far as the current efficiency curves are concerned, high current effi-

Table 1. Properties of the Membranes Applied to the BMED Stacks*

Membrane	Thickness (μm)	IEC (meq/g)	Area resistance ($\Omega \cdot cm^2$)	Selectivity (%)	Voltage Drop (V)	Efficiency (%)
FT-FAB	120	0.8	2–4	>98	—	—
FT-FKB	120	0.8	5–10	>96	—	—
Neosepta BP-1	200	—	—	—	1.2–2.2	>98

*The data are from the product brochure provided by the corresponding company.

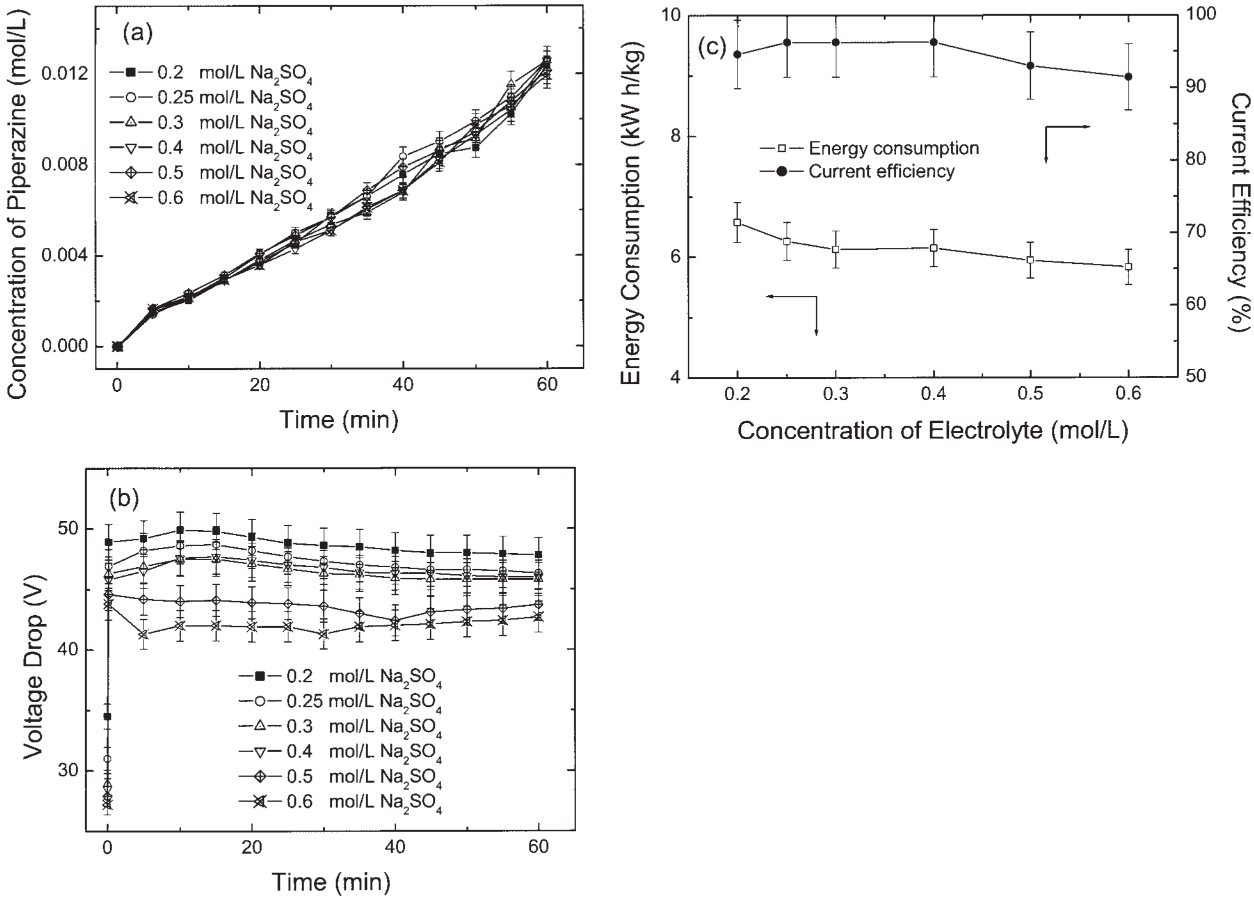


Figure 3. Effect of electrolyte concentration on piperazine regeneration.

(a) Effect of electrolyte concentration on piperazine yield, (b) effect of electrolyte concentration on the voltage drop across the stack, (c) effect of electrolyte concentration on energy consumption and current efficiency. The other operation conditions were current $I = 0.35$A (current density $i = 50$ mA/cm^2), the concentration of Pz·H_2SO_4 $c = 0.13$ mol/L, fluid flow speed $v = 27$ L/h, and configuration Type I.

ciency is only achieved at a concentration range of electrolyte solutions about 0.3~0.4 mol/L.

For the regeneration of piperazine by using BMED, the current efficiency depends on the ratio of current used to generate OH^- by the bipolar membrane, and the ratio of OH^- used to react with piperazine ions (PzH_n^{n+}, n = 1,2). The electrical current cannot be completely taken advantage of, and some of the reasons are as follows: (1) No matter whether it is a bipolar membrane, a cation-selective membrane, or an anion-selective membrane, its selectivity cannot be attained as high as 100%. Therefore, there exists a co-ion flux in every membrane. In this work, the co-ions transported through the anion-selective membrane into the salt compartment are Na^+ in the anode compartment, and H^+ generated in the process of electrolysis; the co-ions transported through the cation-selective membrane into the salt compartment are SO_4^{2-} or HSO_4^- in the base compartment, and OH^- generated by the bipolar membrane; the co-ions transported through the bipolar membrane into neighboring compartments are SO_4^{2-} and HSO_4^- in the cathode compartment and Na^+ and PzH_n^{n+} in the base compartment, respectively. (2) Due to the concentration gradients, all ions and molecules migrate via membranes in the direction towards lower concentrations. (3) Because of the co-ion fluxes and the migration due to concentration gradient, there exist some competitive counter-ions for OH^- and PzH_n^{n+}. That is, OH^-, Na^+, PzH_n^{n+}, SO_4^{2-}, and HSO_4^- are all current carriers in the anion-selective layer of the bipolar membrane; PzH_n^{n+}, Na^+, and H^+ are competitive for the reaction with OH^- generated in the bipolar membrane.

As the electrolyte concentration increases, the osmotic pressure in the solutions neighboring the bipolar membrane increases, which leads to a decrease in water content of the bipolar membrane, thus an increase in the concentration of the membrane's fixed-charged groups, and then an increase in ion selectivity. Therefore, the current efficiency increases because the flux of competitive ions (that is, Na^+, PzH_n^{n+}, SO_4^{2-}, and HSO_4^-) decreases. However, high concentration of electrolyte solutions results in a decrease in current efficiency. First, the high concentration of electrolyte solution leads to a high osmotic pressure, which decreases the water supply into the bipolar membrane[20] and thus limits the water dissociation into the OH^- or H^+. Second, more Na^+ migrates into the salt compartment with the concentration gradient as the driving force, and less piperazine ions can migrate into the base compartment because of the higher ratio of Na^+/PzH_n^{n+} in the salt compartment. And last, the bipolar membrane lying between electrolyte solutions of high concentration has a longer transition time, t_c,[19] which means zero OH^- yield when t is less than t_c.

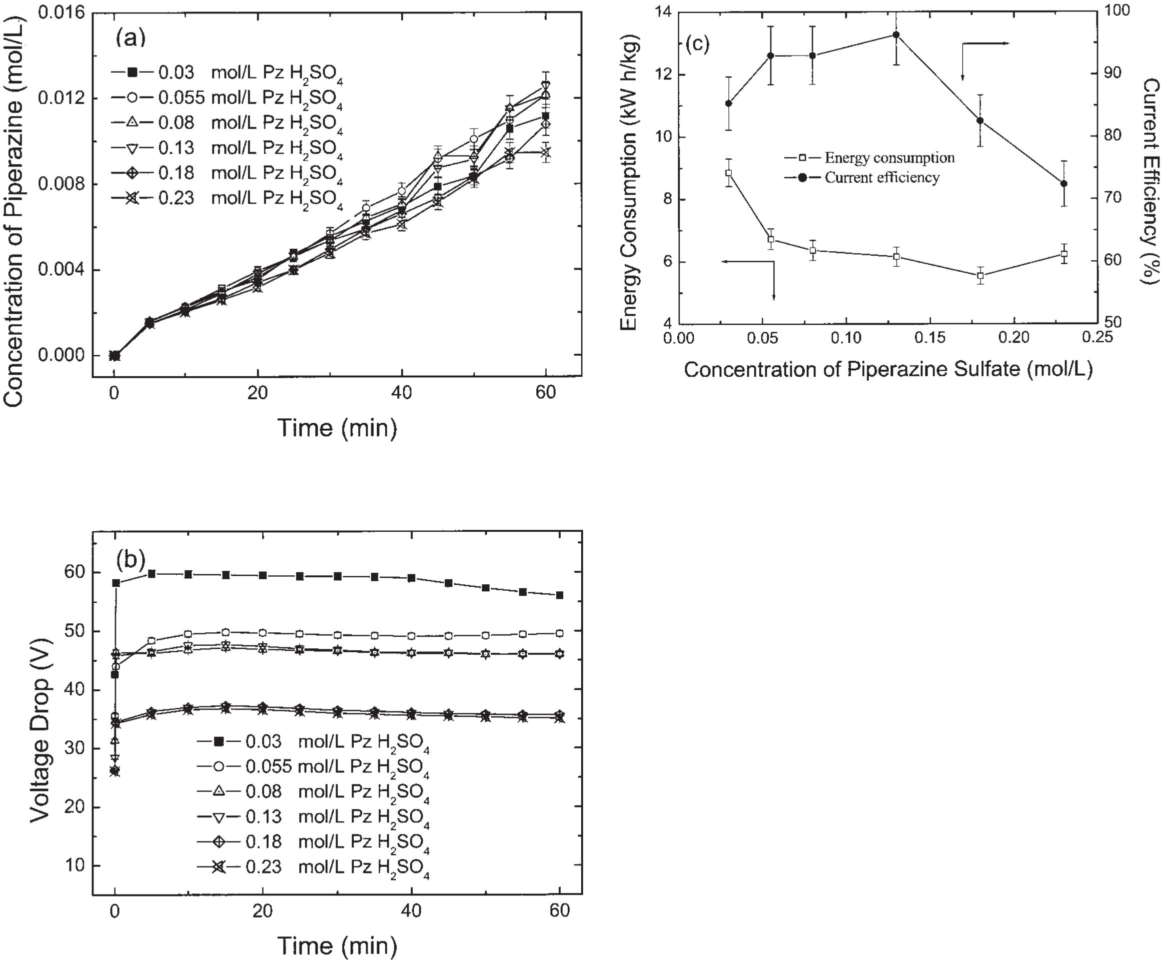


Figure 4. Effect of piperazine sulfate concentration on piperazine regeneration.

(a) Effect of piperazine sulfate concentration on piperazine yield, (b) effect of piperazine sulfate concentration on the voltage drop across the stack, (c) effect of piperazine sulfate concentration on energy consumption and current efficiency. The other operation conditions were current $I = 0.35$ A (current density $i = 50$ mA/cm^2), the concentration of Na_2SO_4 $c = 0.3$ mol/L, fluid flow speed $v = 27$ L/h, and configuration Type I.

Effect of piperazine sulfate concentration on piperazine regeneration

Figures 4a-c show the effects of piperazine sulfate concentration on piperazine yield, the voltage drop across the stack, energy consumption, and current efficiency. There are a lot of similarities among Figure 3 and Figure 4 because both Na_2SO_4 and $Pz{\cdot}H_2SO_4$ are electrolytes in corresponding compartments, but there are some differences. First, the specific conductance of $Pz{\cdot}H_2SO_4$ is less than that of Na_2SO_4, and thus the electrical resistance of $Pz{\cdot}H_2SO_4$ solution accounts for a greater proportion of the total resistance. Therefore, increasing the concentration of $Pz{\cdot}H_2SO_4$ in the salt cycle results in a higher magnitude of the voltage drop decrease. Second, $Pz{\cdot}H_2SO_4$ has a buffering effect on H^+ (see Eq. 2), and thus the pH change in the salt compartment is negligible (pH > 4.8 when $t = 1$ h and $c_0(Pz{\cdot}H_2SO_4) \geq 0.055$ mol/L or so). In the case that the initial concentration of $Pz{\cdot}H_2SO_4$ is 0.03 mol/L, however, the pH decreases dramatically (pH $= 2.83$ when $t = 1$ h) because of the co-ion flux (H^+) transported through the anion-selective membrane from the anode compartment. This leads to an apparent decrease in the total resistance and, thus, the voltage drop in the back part of the voltage drop-time curve. Last, the main reason for the increase of current efficiency is that Na^+/PzH_n^{n+} and H^+/PzH_n^{n+} ratios in the salt compartment decrease as the piperazine sulfate concentration increases. However, there is more piperazine sulfate migrating from the salt compartment due to the concentration gradient, which leads to an osmotic pressure increase of the base compartment and a hydrophobicity increase of the bipolar membrane. There is, thus, a decrease in the current efficiency due to less water being supplied into the bipolar membrane, and energy consumption increases at the much lower current efficiency. The results indicate that the low energy consumption and high current efficiency are achieved when applying piperazine sulfate solution of concentration with a range about 0.08~0.13 mol/L.

Effect of current density on piperazine regeneration

Figures 5a-c indicate that, as current density increases, piperazine yield, the voltage drop across the stack, and energy consumption increase. However, current efficiency decreases and then increases dramatically. In all the experiments, the

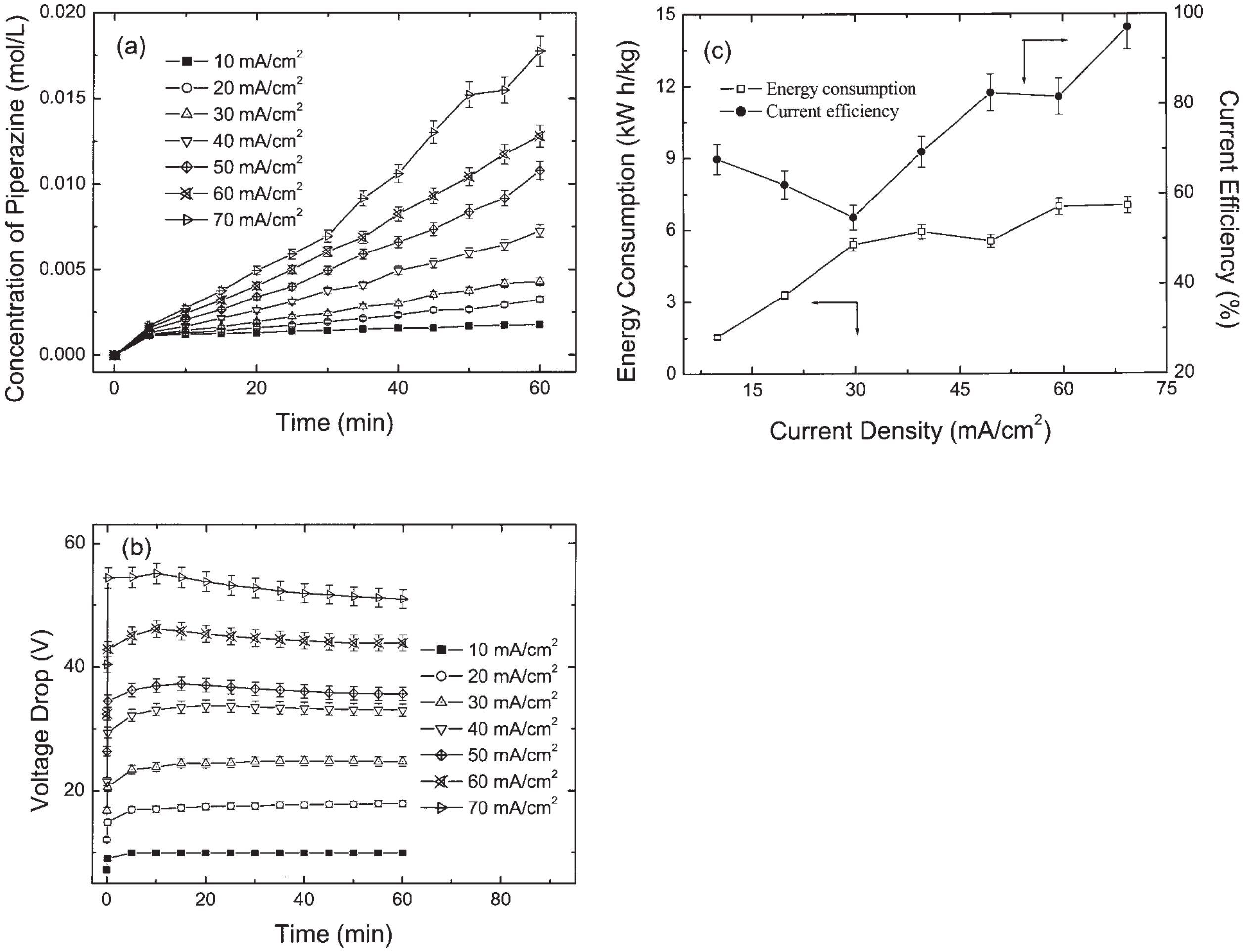


Figure 5. Effect of current density on piperazine regeneration.

(a) Effect of current density on piperazine yield, (b) effect of current density on the voltage drop across the stack, (c) effect of current density on energy consumption and current efficiency. The other operation conditions were the concentration of Na_2SO_4 $c = 0.3$ mol/L, the concentration of $Pz{\cdot}H_2SO_4$ $c = 0.18$ mol/L, fluid flow speed $v = 27$ L/h, and configuration Type I.

voltage drops across the stack at the time when the current was switched off were all less than 4 V, so the irreversible contribution[19,21] (the voltage drop or energy used to overcome the electrical resistance) is much greater than the reversible one. A greater part of the total electrical energy is consumed to overcome the electrical resistance as the current density increases. Whereas the piperazine yield and current efficiency increase, the energy consumption (see Eq. 2) curve tends to level off at higher current densities. When it comes to the current efficiency, there are many factors contributing to the experimental curve. As current density increases, the ion selectivity of all the membranes decreases, which results in a decrease in current efficiency at low current densities. However, a higher current density leads to a shorter transition time (t_c) or less relative salt ion transport,[22] and a less ratio of the piperazine migrating out of the base compartment due to the concentration gradient. Therefore, current efficiency increases steadily at high current densities.

Effect of BMED configuration on piperazine regeneration

As shown in Figures 2a-d, there are four configurations applied to regenerate piperazine by using BMED. Type I, Type II, and Type IV generate piperazine by basifying the piperazine ions (PzH_n^{n+}) from the dissociation of piperazine sulfate with a difference in number of anion or cation selective membranes, and Type III produces piperazine by replacing the anions of piperazine sulfate (SO_4^{2-} and HSO_4^-) with OH^- generated in the bipolar membrane. The effect of BMED configuration on piperazine regeneration can be attributed to the ion transport and molecular diffusion in different compartments.[23]

Figure 6a shows the effect of BMED configuration on piperazine yield. The results indicate piperazine yield increases in the order: Type III < Type I < Type II ≈ Type IV. The reason why the initial piperazine concentration, in the case of Type III, is much higher than that of any other configuration, is that there exists some piperazine in the salt compartment before a current is applied due to the hydrolysis of piperazine sulfate.

Figure 6b shows the effect of BMED configuration on the voltage drop across the stack. For Type II, its voltage drop is higher than that of Type I in the certain amount of time after a current is switched on, although the BMED stack of Type II configuration has less membranes and compartments. This is mainly because the electrical resistance of the anode compartment increases sharply when piperazine sulfate is used as the

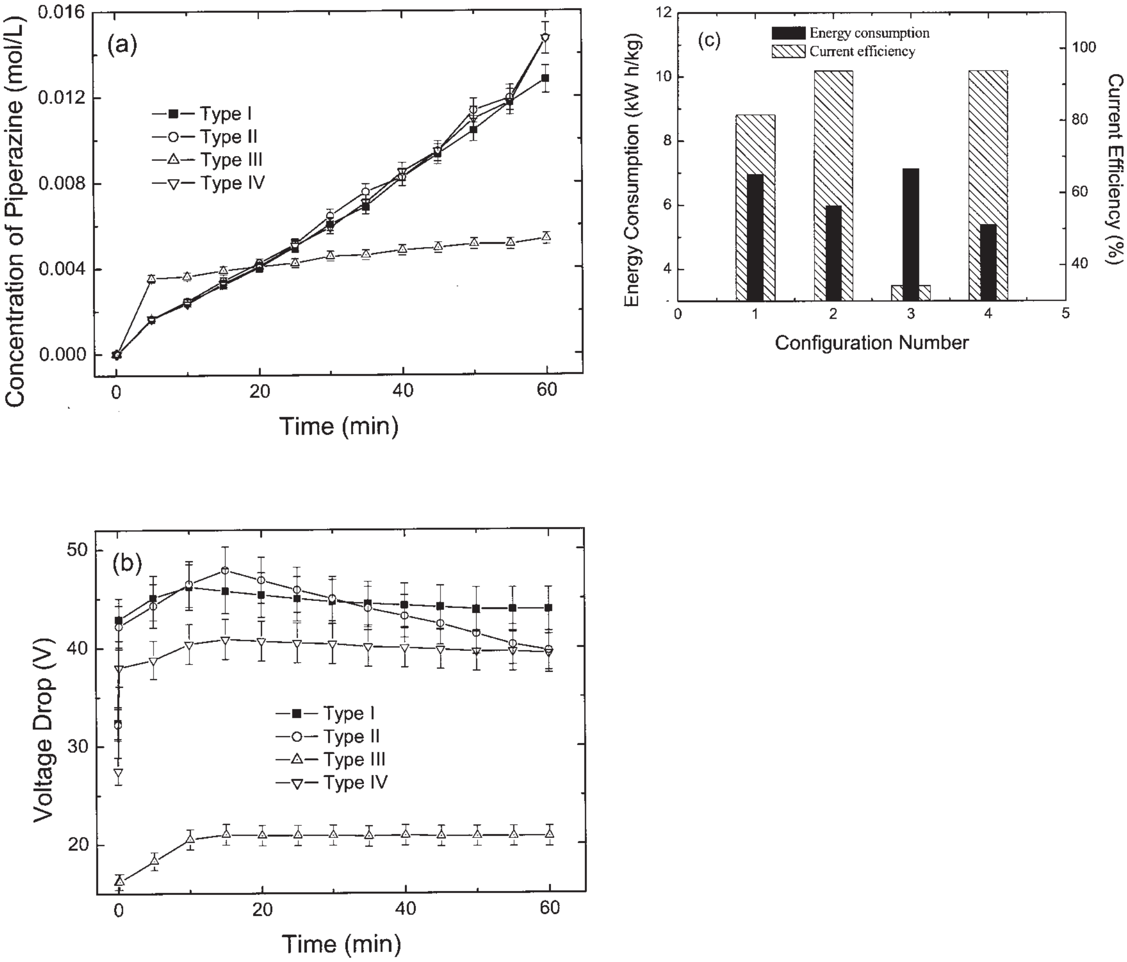


Figure 6. Effect of configuration on piperazine regeneration.

(a) Effect of configuration on piperazine yield, (b) effect of configuration on the voltage drop across the stack, (c) effect of configuration on energy consumption and current efficiency. The other operation conditions were current $I = 0.42$ A (current density $i = 60$ mA/cm^2), the concentration of Na_2SO_4 $c = 0.3$ mol/L, the concentration of $Pz{\cdot}H_2SO_4$ $c = 0.18$ mol/L, and fluid flow speed $v = 27$ L/h.

anode rinsing electrolyte and a certain amount of volume of the compartment is occupied by the gas bubbles. However, the voltage drop decreases steadily when there is more and more H^+ generated in the process of electrolysis. For Type III, the BMED stack of that configuration has less membranes and compartments than that of Type I configuration, and its voltage drop is the lowest. For Type IV, the BMED stack of that configuration has the same number of membranes and compartments as that of Type I configuration, but its voltage drop is lower. The H^+, which is generated in the process of electrolysis, can easily migrate through the cation-selective membrane into the salt compartment and decrease the electrical resistance.

Figure 6c shows the effect of BMED configuration on energy consumption and current efficiency. The results indicate that energy consumption increases in the order: Type IV $<$ Type II $<$ Type I $<$ Type III, and current efficiency in the order: Type III $<$ Type I $<$ Type II $\approx$ Type IV. Among the four BMED configurations, Type III has the lowest current efficiency and highest energy consumption because the H^+, migrating from the anode compartment, is easily accessible to the piperazine or OH^- in the salt/base compartment, thus much less piperazine is regenerated. Type IV has the highest current efficiency and lowest energy consumption because in the buffering range of piperazine sulfate, a certain amount of H^+ leads to an increase in PzH_n^{n+} ions in the salt compartment without an increase in H^+/PzH_n^{n+} ratio. For the same reason, Type II also has a high current efficiency and lower energy configuration.

Process economics

The process cost varies with the operation conditions and capacity; thus, the following cost estimation is made on the basis of the laboratory-scale experimental equipment under the conditions shown in Table 2. The corresponding calculation was conducted by the method reported in literature.[24] As seen in Table 2, the process cost for the regeneration of piperazine is \$0.96/kg Pz with a laboratory-scale equipment, which is much less than the current market price of piperazine (ca. \$31/kg $Pz{\cdot}6H_2O$ available in China). It should be noted that the process will become more economical for application on a pilot scale or industrial scale because both the energy cost and investment cost will decrease with an increase in production

Table 2. An Estimation of the Process Cost

Operation Conditions	
Current density	$i = 60$ mA/cm^2
Effective membrane area	$A = 7.07$ cm^2
The concentration of Na_2SO_4	$c_0(Na_2SO_4) = 0.3$ mol/L
The concentration of $Pz \cdot H_2SO_4$	$c_0(Pz \cdot H_2SO_4) = 0.18$ mol/L
Fluid flow speed	$v = 27$ L/h
Stack configuration	BP-C-C (Type IV)
The energy consumption	$E = 5.4$ kW · h/kg Pz
The process capacity	5.55 kg Pz/year
Energy Cost	
Electricity charge	\$0.10/kW · h
The energy cost for the regeneration	\$0.54/kg Pz
The energy cost for the peripheral equipment	\$0.02/kg Pz
The total energy cost	\$0.56/kg Pz
Investment Cost	
Membrane life-time and the amortization of the peripheral equipment	3 years
Membrane prices	\$135/m^2 mono-polar membrane; \$1350/m^2 bipolar membrane
Membrane cost	\$1.15
Stack cost (including membrane cost)	\$1.72
Peripheral equipment cost	\$2.58
Total investment cost	\$4.30
Amortization	\$1.43/year
Interest	\$0.34/year
Maintenance	\$0.43/year
The total fixed cost	\$2.20/year or \$0.40/kg Pz
The Total Process Cost	\$0.96/kg Pz

capacity; furthermore, the operation will become more stable. Therefore, the process is not only scientifically novel but also economically feasible and attractive besides its potential environmental benefits.

Conclusions

An experimental study was carried out on the regeneration of a flue-gas desulfurizing agent by using BMED. The focus is on the effects of electrolyte concentration, piperazine sulfate concentration, current density, and BMED configuration on piperazine regeneration. The results indicate that low energy consumption and high current efficiency are achieved when applying electrolyte solutions with a concentration range about 0.3~0.4 mol/L, piperazine sulfate solution with a concentration range about 0.08~0.13 mol/L, and BMED stack of BP-C-C configuration. The results also indicate that when applying a high current density to the BMED stack, it has high current efficiency and energy consumption. The process cost is estimated to be \$0.96/kg Pz for the regeneration of piperazine with the laboratory-scale experimental equipment.

The co-ion flux is considered as an unfavorable factor for high current efficiency. It is true of most of the experiments in this work. However, a certain amount of H^+ flux can improve current efficiency in the case of the BMED stack of BP-C-A configuration because it increases the amount of PzH_n^{n+} ions in the salt compartment without an increase in H^+/PzH_n^{n+} ratio in the buffering range of piperazine sulfate. In that sense, the ion selectivity of anion-selective membrane does not need to be too high when applied to regenerate piperazine by using a BMED stack of BP-C-A configuration.

There is no doubt about the feasibility of regenerating the flue-gas desulfurizing agent by using BMED. Furthermore, such method is available for not only piperazine, but also for other amine solvents as long as the formed amine sulfate can be disassociated into amine cations, but the operation efficiency and the process economics have to be testified to with experiments.

Acknowledgments

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