Recovery of $HgCl_2$ Using Cl^--Form Ion Exchanger

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Mercury and mercury compounds have been used widely in electrolytic processing or as catalysts in chemical processes. Although they are used in closed systems, a large amount of mercury is still being discharged to the environment. Furthermore, a new big problem involving mercury has arisen: the garbage gathered from living environments contains an unbelievably large amount of mercury, which originates from broken thermometers and waste batteries. When the garbage is burned, the mercury vaporizes into the flue gas. The mercury vapor is recovered by washing the flue gas with acid, resulting in $HgCl_2$ in the acid solution. This solution is usually neutralized with NaOH.

It is, therefore, important to find a way in which $HgCl_2$ may be recovered from a mixed aqueous solution of ($HgCl_2$ + NaCl), ($HgCl_2$ + HCl), or ($HgCl_2$ + NaCl + HCl). Kataoka and Yoshida (1988) showed that $HgCl_2$ was adsorbed strongly on Cl^--form anion exchanger by using the following complex formation reactions:

$$R \cdot Cl^- + HgCl_2 \rightleftharpoons R \cdot HgCl_3^- \qquad (1)$$

$$2R \cdot Cl^- + HgCl_2 \rightleftharpoons R_2 \cdot HgCl_4^{2-} \qquad (2)$$

$$R \cdot HgCl_3^- + HgCl_2 \rightleftharpoons R \cdot Hg_2Cl_5^- \qquad (3)$$

The selectivity for the adsorption of $HgCl_2$ was extremely high, even in the case where NaCl and/or HCl (such as 5 mol/dm^3) were present in the solution. The maximum adsorption rate of $HgCl_2$ was twice as great as the exchange capacity of the resin.

Since the binding between $HgCl_2$ and Cl^--form resin is very strong, large amounts of eluent, such as concentrated NaCl or HCl solution, may be necessary when using the normal desorption process. To increase the desorption rate and to reduce the final resin-phase concentration of Hg(II), a method of electrolytic desorption of mercury from $HgCl_2$–Cl^--form resin complex was used. The effects of electric current, temperature and the concentration of eluent on the desorption rate and on the final resin-phase concentration of Hg(II) are discussed. The gel- and porous-type exchangers were used in this experimental study. Also tested were the type of resins suitable as the $HgCl_2$ adsorbent.

Experimental

The systems and conditions used in this experimental study are given in Table 1. Two strong base resins were used: SA10A (gel-type resin) and PA416 (porous-type resin). The $HgCl_2$–Cl^--form resin complex were prepared by batch method: the resin particles of Cl^--form were contacted with 0.2 mol/dm^3 $HgCl_2$ aqueous solution in a flask. After reaching an equilibrium, the resin particles were washed with deionized, distilled water and dried at room temperature. The initial resin-phase concentration of Hg(II), Q(mol/kg), and the exchange capacity Q_o(mol/kg) are shown in Table 1. Q/Q_o was nearly equal to 1.5 for both ion exchangers. In addition, the resin was not saturated by $HgCl_2$, because when the resin is saturated, Q/Q_o is equal to 2 (Kataoka and Yoshida, 1988).

Figure 1 shows the experimental apparatus and the electrode. The electrolytic cell is made of Pyrex glass, 45 mm in diameter and 65 mm deep. The electrode and the wire are platinum, with the electrodes separated by a distance of 30 mm in the electrolytic cell. The cell contained 50 cm^3 of eluent (NaCl or HCl aqueous solution) which was stirred thoroughly by magnetic stirrer and maintained at a constant temperature by the jacket. The dry resin particles (0.5 g) of $HgCl_2$–Cl^--form resin complex were thrown into the solution and electricity was turned on simultaneously. The need to change the resin-phase concentration of Hg(II) was determined by the following steps: after a period of time, 2 cm^3 of the solution was removed and the cathode was exchanged for a new one simultaneously. The removed solution was analyzed for mercury. The cathode, which was dried by a drier at room temperature for about 30 minutes, was weighted to obtain the amount of the mercury deposited on it. The resin-

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Table 1. Experimental Systems and Conditions

Fig. No.	Resin	Form	Eluent	Concentration of Eluent (mol/dm^3)	Current Density (A/cm^2)	Temperature (K)
—	*Strong anion*	$HgCl_2$—Cl^--form				
3	DIAION SA10A*(gel-type)	resin complex	HCl	1	0, 0.5	298
2			NaCl	2	0, 0.25, 0.5	298
3			NaCl	0.5, 1, 2, 3, 5	0.5	298
4, 5, 6			NaCl	2	0.5	298, 323, 340
4	DIAION PA416** (porous-type)		NaCl	2	0.5	298, 323, 340

*Q_o = 1.77 mol/kg; Q = 2.63 mol/kg
**Q_o = 2.17 mol/kg; Q = 3.28 mol/kg

phase concentration of mercury was calculated according to the mass balance using the solution concentration of $HgCl_2$ and the mercury deposited on the cathode.

The concentration of Hg(II) in the solution was measured by the plasma spectroscopy (SMI Spectraspan III) and by replacing titration with Mg-EDTA and chelating agent 0.01 M disodium EDTA.

Results and Discussion

Figure 2 shows the effect of the current density on the desorption rate for SA10A; the value of the initial resin-phase concentration of Hg(II), Q(mol/kg) in Table 1. The eluent was 2 mol/dm^3 NaCl and the temperature 298 K: the desorption rate increases with an increase of the current density. Of the resins, desorption rate for 0.5 A/cm^2 was the highest.

Figure 3 shows the effect of the NaCl concentration on the desorption rate for SA10A with the current density of 0.5 A/cm^2 and the temperature 298 K. When the concentration of NaCl was 2 mol/dm^3, the desorption rate was the highest. Above a NaCl concentration of 2 mol/dm^3, any increase in NaCl slowed the desorption rate, due to the increase in the NaCl electrolysis which accompanies increased concentration. These results suggest that the most favorable concentration of NaCl may be 2 mol/dm^3. The elution curve obtained by using the HCl eluent is also shown in Figure 3. The concentration of HCl was 1 mol/dm^3 and the current densities were 0 and 0.5 A/cm^2. Since the desorption rate for NaCl (1 mol/dm^3 and 0.5 A/cm^2) is faster than that for HCl (1 mol/dm^3 and 0.5 A/cm^2), NaCl may be better than HCl as the eluent. In the case of HCl, Figure 3 shows that there is little difference between the desorption curves for 0 and 0.5 A/cm^2, that is, almost all current is used, not for the electrolysis of $HgCl_2$, but for the electrolysis of HCl.

It is expected that temperature should increase the desorption rate, Figure 4. The resins were SA10A(gel-type) and PA416(porous-type), the current density was 0.5 A/cm^2, and the concentration of NaCl was 2 mol/dm^3. The desorption rate at 340 K was relatively higher than that at 298 K. The desorption rate for PA416 was faster than that for SA10 at 298 K but there was little difference between them at 323 and 340 K. The heatproof temperature of Cl^--form of SA10A and PA416 is 333 K. However, the deterioration was not recognized in our experiment even at 340 K. Since the period of desorption time was relatively short, (only 100 min to reach nearly the final equilibrium), deterioration may not be serious, even at the heatproof temperature.

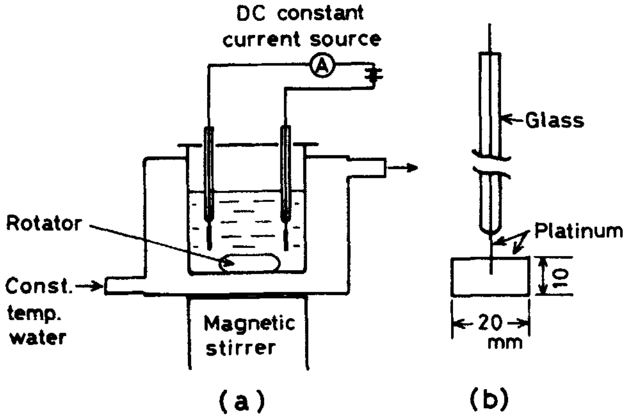

Figure 1. Experimental apparatus: (a) electrolytic cell and (b) electrode.

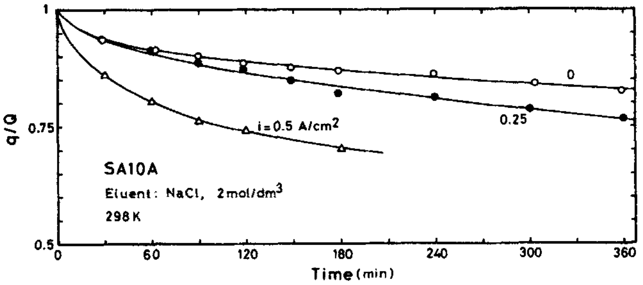

Figure 2. Effect of current density on electrolytic desorption.

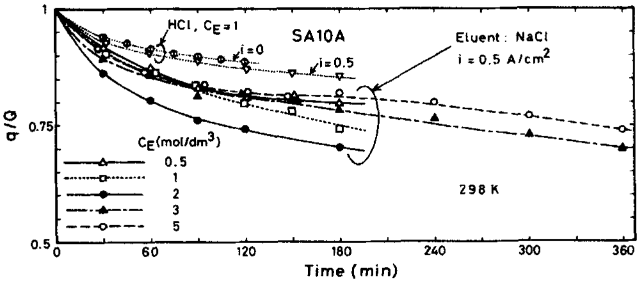

Figure 3. Effect of the concentration of eluent on electrolytic desorption.

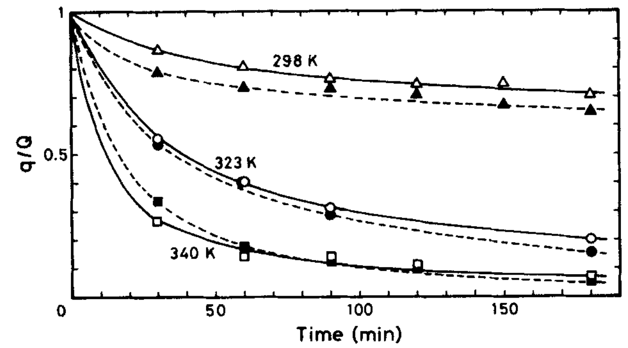

Figure 4. Effect of temperature on electrolytic desorption.
(△, ○, □, SA10A; ▲, ●, ■, PA416)

Figure 5 shows the change in weight of the mercury deposited on the cathode with time. It is significantly influenced by the temperature. The higher the temperature is, the more and the faster mercury deposits on the cathode: for example, when the time is 90 min, the weight of the deposited mercury at 340 K is about 10 times as heavy as that at 298 K.

Figure 6 shows the concentration history of Hg(II) in the solution. The higher the temperature is, the earlier the peak arises. The temperature effect on the concentration history is less than that on the deposition rate of mercury on the cathode with time. When the temperature is higher than 323 K, the desorption rate may be approximated by the deposition rate of mercury on the cathode. The mathematical model for the desorption process has not been developed, because the intraparticle mass transfer mechanism of $HgCl_2$ has not been clear. When $HgCl_2$–Cl^--form resin complex makes contact with NaCl solution, $HgCl_2$ is desorbed from the resin into the solution. Since in the early stage the desorption rate is higher than the deposition rate, the concentration of $HgCl_2$ increases. However, the desorption rate slows down immediately, because of the very favorable equilibrium isotherm for adsorption of $HgCl_2$, even in the case of high concentration of NaCl. Eventually, the deposition rate becomes faster than the desorption rate and the concentration of $HgCl_2$ decreases. Finally, when the concentration of $HgCl_2$ is decreased by the electrolysis, the desorption rate accelerates once more.

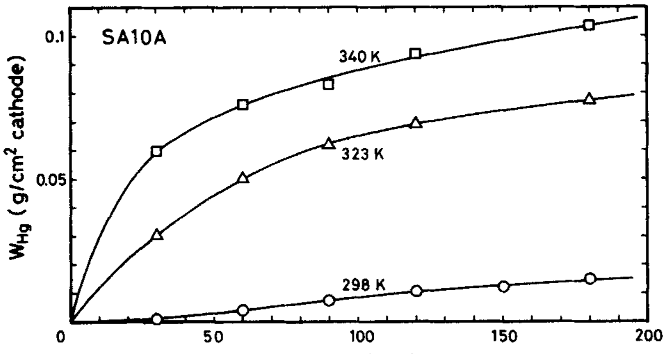

Figure 5. Weight change of mercury deposition on cathode with time.

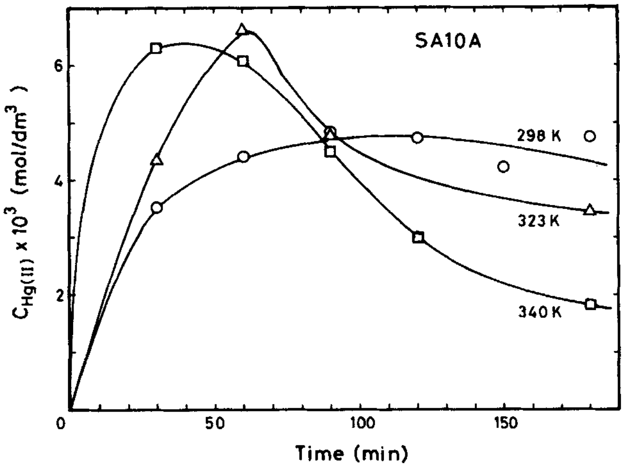

Figure 6. Concentration history in electrolytic cell.

From these results, the removal of $HgCl_2$ by adsorption on Cl^--form anion exchanger and the regeneration of $HgCl_2$–Cl^--form resin complex to Cl^--form resin with mercury metal simultaneously recovered by electrolysis, this method seems possible. However, more detailed experimental and theoretical study on the kinetics and the dynamics should be done in the future.

Notation

C_E = concentration of eluent, mol/dm³
$C_{Hg(II)}$ = liquid-phase concentration of Hg(II), mol/dm³
i = current density, A/cm²
Q = initial resin-phase concentration of Hg(II), mol/kg
Q_o = exchange capacity of ion exchanger, *eq*/kg
q = resin-phase concentration, mol/kg
W_{Hg} = weight of mercury deposited on cathode, g/cm²

Literature Cited

Kataoka T., and H. Yoshida, "Adsorption of $HgCl_2$ on Cl^--form Anion Exchangers—Equilibrium Isotherm," *Chem. Eng. J.*, **37**, 107 (1988).

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