Original Paper

Cu Recovery from Industrial Wastewater Via Low Temperature Combustion of Cu-loaded Brown Coal

Atsushi YOSHINO, Hidenari HORI, Kazuyoshi SATO, and Takayuki TAKARADA

(Received September 24, 2013)

The etching process by copper chloride is widely used in printed wiring board manufacturing. Unfortunately, almost copper waste solution is treated by neutralization method and the precipitated sludge is dumped on the ground without copper recovery. Brown coal has ion exchange ability because it has carboxy groups and hydroxyl groups in it.

Using that ability of brown coal, copper recovery from the waste etching solution by low energy consumption method is studied. Copper ion in the waste solution can be loaded on Loy Yang brown coal around 8.5 wt% by adding ammonium hydroxide, adjusting pH in 9-11.5 and stirring at room temperature. When pH range is in 9-11.5, it is considered that copper and ammonium complex ions such as tetraamminecopper(II) ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ are produced and exchanged with proton of carboxy groups in brown coal. Cu-loaded brown coal can be burnt at extremely low temperature; 160-180°C, and 0.5-1.0 μm copper oxide particles are formed as the residue. From XRD analysis at the middle of burning, it is considered that Cu_2O plays a role of catalyst of gasification and/or oxidation. It was shown that low energy consuming copper recovery method is feasible by using capability of ion exchange of brown coal and catalysis of Cu-loaded brown coal.

塩化銅系エッチング液を用いたエッチングプロセスはプリント配線板製造業において広く用いられている。そのエッチング廃液は一般に中和法により処理されるため、沈澱物のスラッジは銅回収が行われずに埋め立て処理されてしまっている。一方、褐炭はカルボキシル基や水酸基を多く含有しているため、イオン交換能を有している。そこで褐炭のイオン交換能を活用し、エッチング廃液からの低エネルギー消費での銅回収法を検討した。エッチング廃液に水酸化アンモニウムを添加して pH を 9-11.5 の範囲に調整し、室温で褐炭と攪拌混合することで廃液中の銅イオンを Loy Yang 褐炭に約 8.5 wt% 担持させることができた。pH が 9-11.5 の範囲にある場合、テトラアンミン銅(II)イオン $[\text{Cu}(\text{NH}_3)_4]^{2+}$ 等の錯イオンが生成し、褐炭中のカルボキシル基のプロトンとイオン交換すると考えられる。また銅担持褐炭は 160-180°C と極めて低温で燃焼し、その残渣として 0.5-1.0 μm の酸化銅微粒子が得られた。その燃焼途中で採取したサンプルの XRD 分析から、 Cu_2O がガス化や酸化触媒として作用していると推定できる。これにより、褐炭のイオン交換能と銅担持褐炭の触媒作用を活用した低エネルギー消費での銅回収法の実現可能性を見出した。

Key Words

Copper recovery, Brown coal, Wastewater, Low temperature combustion, Catalyst

1. Introduction

The etching process by copper chloride is widely used in printed wiring board manufacturing. Unfortunately, almost copper waste solution is treated by neutralization method and the precipitated sludge is dumped on the ground without copper recovery. Electrolysis method is also used in order to recover copper from the waste solution, but it consumes a lot of energy, so it is not suitable for closed

recycle system in site.

Even though the estimated amount of deposits is huge, brown coal is not available because of the high water contents and its low calorific value. However, brown coal has ion exchange ability because it has carboxy groups and hydroxyl groups in it.

Nickel loaded Loy Yang brown coal has been studied as an outstanding gasification catalyst^{1) ~ 10)}. It has been come out that Nickel is loaded on Loy Yang brown coal by ion exchange, Ni-loaded brown coal works on the gasification catalyst, and also Nickel oxide fine particles are

Department of Chemical and Environmental Engineering,
Gunma University
1-5-1 Tenjin-cho, Kiryu-shi, Gunma 376-8515, Japan

produced by burning at low temperature around 200°C.

Using that ability of brown coal, copper recovery from the waste etching solution by low energy consumption method is studied.

2. Experimental

2.1 Materials

As the medium of recovering copper ion from the waste solution, Loy Yang brown coal from Australia which is sifted in 200-325 mesh is used.

Table 1 and Table 2 show proximate and ultimate analysis of Loy Yang brown coal. De-ashed coal is prepared by stirring 60°C, 1hr with 5 M HCl twice, 12 M HF once; stirring with acid, dewatering by suction filtration, washing by deionized water, and dried by an oven at 107°C, 6 hrs in N₂ atmosphere. Ash content of the de-ashed brown coal is 0.017 wt%.

Copper chloride waste etching solution (which is named ETS (Cl)) of printed wiring board manufacturing process is provided by Hitachi Chemical (Table 3).

2.2 Copper loading method

Copper loading method is summarized in Fig. 1. After the pH of ETS (Cl) is adjusted by adding ammonium hydroxide, dried Loy Yang coal is added in the solution; brown coal 1 g; ETS (Cl) 0.2 g, and stirring 24 hrs at room temperature. Then it is dewatered by suction filtration, washed by deionized water, dried by an oven at 107 °C, 6 hrs in N₂ atmosphere.

Dried Cu-loaded brown coal is milled and sifted in 200-325 mesh.

2.3 Formation method of copper oxide fine particles

Dried Cu-loaded brown coal 1 g is put in a square tray, heated in an electric muffle furnace by the condition; ramp1 RT-500 °C /45 min, ramp2 500-815 °C /60 min, hold 815°C, 60 min based on JIS M8812 method.

Table 1 Proximate analysis of Loy Yang brown coal [wt%]

Moisture	Fixed Carbon (diff.)	Volatile Matter	Ash
18.17	27.33	53.84	0.66

Table 2 Ultimate analysis of Loy Yang brown coal [wt%]

C	H	N	S	O (diff.)
65.92	4.75	0.74	0.11	28.48

Table 3 Main component of ETS (Cl) [wt%]

Cu	Cl	pH
12	13	< 1

Fig. 1 The outline of copper loading method

2.4 Evaluation methods

Copper loading of brown coal is measured by Atomic absorption spectrophotometer; Shimazu AA-6400F. Copper loaded on brown coal is extracted by 1M nitric acid 3 times and diluted by deionized water into AA measurement range. Morphological studies of burnt ash are analyzed by XRD; MAC M03XHF22 and RINT RAPID. Particle shape is observed by FE-SEM; JEOL JSM-6700F. Copper loading structure is analyzed by XPS; Rigaku Smart Lab.

3. Results and Discussion

3.1 Copper loading on brown coal from ETS (Cl)

3.1.1 pH effect on Copper loading

pH effect on Copper loading is summarized in Fig. 2. It shows around 8.5 wt% of Cu can be loaded on Loy Yang brown coal by ion exchange method when pH is within 9-11.5. The most left point shows the data which pH is not adjusted, when the original ETS (Cl) solution is used.

Fig. 2 Effect of pH on Copper loading

The mechanism of the ion exchange is presumed that carboxy groups in brown coal exchange the protons and complex cations; for example $[\text{Cu}(\text{NH}_3)_4]^{2+}$ as below ¹¹⁾.

So, in the low pH condition, concentration of proton is too high, the equilibrium reaction can't go right further. When pH range is between 2.5 to 8.8, copper ion is react with hydroxyl ion, then $\text{Cu}(\text{OH})_2$ particles are precipitated. When pH is increased over 8.8, $\text{Cu}(\text{OH})_2$ particles are dissolved again, then copper and ammonium complex ions such as tetraamminecopper(II) ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ are produced. Therefore, the pH range which is larger than 9 is suitable to exchange copper ion by brown coal. Cu-loaded brown coal is measured by XPS analysis in order to study the Cu-loading mechanism, the result is shown in Fig. 3. After loading, COOH and NH_3 binding energies are shifted and Cu(II)-N bond is detected. So copper and ammonium complex ion could be exchanged with protons of carboxy group. At Cu(2p) spectra, Cu (II)-N, $\text{Cu}(\text{OH})_2$ and Cu_2O spectra are identified by wave form separation. Therefore ion exchange is not only mechanism of the Copper loading, but also $\text{Cu}(\text{OH})_2$ particle deposition and physical absorption are possible mechanisms.

3.1.2 Stirring time effect on Copper loading

Time dependency in Copper loading process is

evaluated until 1440 min. Fig. 4 shows that only 5 min stirring is enough to exchange copper ion and the Copper loading is around 10.5 wt%. Shorter time shows higher Copper loading than longer time. Since neutralization reaction of adding ammonium hydroxide is exothermic, in the case of shorter stirring time, the solution temperature shows higher than longer time. Therefore, the endothermic equilibrium reaction Eq. (1) is go right way.

3.1.3 Repetition effect on Copper loading

Table 4 shows the results of repetition loading. After the first time loading, new brown coal is added in the filtrate. And also another brown coal is added in the 2nd

Fig. 4 Stirring time effect on Copper loading

Fig. 3 XPS spectra of Brown coal and Copper Loaded Brown coal

Table 4 Repetition effect on Copper loading

Item		1st time loading	2nd time loading	3rd time loading
Before Loading	Cu content in ETS(Cl) [g]	1.028	0.590	0.183
	pH	9.60	9.54	8.95
	Brown coal added[g]	5.05	5.04	5.07
After Loading	Cu-loading on Brown coal [g]	0.438	0.407	0.152
	[wt%]	8.68	8.08	3.00
	Cu content in Filtrate [g]	0.590	0.183	0.031
	pH	9.54	8.95	7.54

filtrate. At the 3rd time loading, copper is still remaining in the filtrate, in spite of enough brown coal is added. One reason might be the lowered pH than 8.8 at the loading process. Whether if copper recovery is available at low copper concentration, diluted ETS (Cl) solution is tested.

3.1.4 Copper loading from diluted ETS (Cl) solution

Low copper concentration 1, 10 ppm solutions are prepared by diluting the original ETS (Cl) solution. Copper concentrations of these filtrates after ion exchange are 0.002, 0.003 ppm respectively. So, copper recovery from low copper concentration solution by brown coal is also available.

3.2 Formation of copper oxide fine particles from Cu-loaded brown coal

3.2.1 Analysis of the residue of burnt Cu-loaded brown coal

Dried Cu-loaded brown coal whose copper loading is 8.56wt% is burnt at 815°C under condition of JIS M8812 method. Fig. 5 shows the SEM image and Fig. 6 shows the XRD spectra of the residue of burnt Cu-loaded brown coal. These data show that the size of particles is around 0.5-1.0 μm , the chemical formula is CuO. The content of CuO in the residue is 91.8 wt%. When de-ashed brown coal is used for Copper loading, the content of CuO in the residue is increased to 98.8 wt%.

3.2.2 Weight loss curve of Cu-loaded brown coal

Weight loss curves are measured by thermogravimetric

Fig. 5 SEM image of Cu-loaded Loy Yang Brown Coal (Cu-loading 8.56 wt%), Ash burning process at 815°C

Fig. 6 XRD spectra of Cu-loaded Loy Yang Brown Coal (Cu-loading 8.56wt%), Ash burning process at 815°C

Fig. 7 Weight loss curves of Cu-loaded brown coal (Cu-loading 8.56 wt%, de-ashed) and Ni-loaded brown coal (Ni-loading 8.8 wt%, de-ashed)

analysis; TG. Fig. 7 shows the results of TG of Cu-loaded brown coal; Copper loading 8.56 wt%, de-ashed, and Ni-loaded brown coal; Nickel loading 8.8 wt%, de-ashed.

At the beginning, the weight of Cu-loaded brown coal is gradually decreased by moisture evaporation. At 160-180°C rapid weight decrease is shown, and the weight loss is finished within 3-5 min.

Dotted line shows the weight loss curve of Ni-loaded brown coal, the start temperature of rapid decrease is 200-210°C. In usual coal combustion, volatile matter is released and burnt at 400-600°C. So, it is considered that copper and nickel play a role of a catalyst of gasification and/or oxidation. It is

found that Cu-loaded brown coal can be burnt extremely low temperature; 160-180°C, which is lower than the temperature of Ni-loaded brown coal. Samples are taken at ① before heating, ② at 165°C and ③ at 180°C during burning shown in Fig. 7. Fig. 8 shows the photos, and Fig. 9 shows XRD spectra of these samples. ② sample shows reddish-brown color, on the other hand ③ sample shows black color in Fig. 8.

② sample shows Cu₂O spectra by XRD analysis, on the other hand ③ sample shows CuO spectra in Fig. 9. So it's obvious that Cu₂O plays a role of catalyst of gasification and/or oxidation of brown coal^{12)~15)}.

Then another TG analysis is tested in order to understand the formation mechanism of Cu₂O particles. Temperature ramp is 10 °C /min and heating is stopped at 25, 50, 75 and 100% weight decrease. Fig. 10 shows the results of XRD analysis. At 25% weight loss (a), only Cu is detected. At 50% loss (b), Cu and Cu₂O are detected, and at 75% loss (c), Cu₂O, CuO and small peaks of Cu are detected. Finally at 100% loss (d), only CuO is detected. This results shows Cu captured by carboxy group is reduced and crystallized at initial stage when volatile matters are released, then the Cu particles are oxidized to Cu₂O and finally to CuO.

Therefore, in the burning process copper is formed as below,

Fig. 8 Photos during burning Cu-loaded de-ashed Loy Yang Brown Coal(Cu-loading: 8.56 wt%) at simulated air atmosphere; ① before heating, ② at 165°C and ③ at 180°C

Fig. 9 XRD spectra of ② at 165°C and ③ at 180°C

Fig.10 XRD spectra of Cu-loaded Loy Yang Brown Coal, a) 25%, b) 50%, c) 75% and d) 100% weight loss, when ramp is 10°C / min of TG analysis

Fig. 11 SEM image of ③ particles sampled at 180°C of Fig. 7

SEM image of the residue taken at 180°C, ③ sample of Fig. 7, is shown in Fig. 11. The particle size is around 0.5-1.0 μm and the shape is cubic. Cubic shape suggests that the crystal is the cubic lattice structure and it is formed as Cu and/or Cu_2O crystal.

Comparing the shape with the particles taken at 815°C in Fig. 5, the angles are rounded when burning temperature is 815°C. This means these particles are partially fused and sintered each other where the ambient temperature is 815°C.

4. Conclusion

Copper recovery by using Loy Yang brown coal from waste etching solution of printed wiring board manufacturing is studied.

1. It was found that copper ion in the waste solution can be loaded on Loy Yang brown coal around 8.5 wt% by adding ammonium hydroxide, adjusting pH in 9-11.5 and stirring at room temperature. When pH range is in 9-11.5, it is considered that copper and ammonium complex ions such as tetra-amminecopper(II) ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ are produced and exchanged with proton of carboxy groups in brown coal, and copper is highly dispersed in brown coal.
2. It was also found that Cu-loaded brown coal can be burnt at extremely low temperature; 160-180°C, and 0.5-1.0 μm copper oxide particles are formed as the residue.

Since XRD spectra of the sample taken at 165°C shows Cu_2O , it is considered that Cu_2O plays a role of catalyst of gasification and/or oxidation.

Therefore it was shown that low energy consuming copper recovery method is feasible by using capability of ion exchange of brown coal and catalysis of Cu-loaded brown coal.

References

- 1) Le, D.; Xiao, X.; Morishita, K.; Li, L.; Takarada, T., *J. of Chem. Eng. of Japan*, **43**, 443-450 (2010)
- 2) Li, L.; Morishita, K.; Mogi, H.; Yamasaki, K.; Takarada, T., *Fuel Processing Technology*, **91**, 889-894 (2010)
- 3) Meesuk, S.; Cao, J.; Sato, K.; Ogawa, Y.; Takarada, T., *Energy Fuels*, **25**, 4113-4121 (2011)
- 4) Meesuk, S.; Cao, J.; Sato, K.; Ogawa, Y.; Takarada, T., *Energy Fuels*, **25**, 5438-5443 (2011)
- 5) Meesuk, S.; Cao, J.; Sato, K.; Ogawa, Y.; Takarada, T., *J. of Analytical and Applied Pyrolysis*, **94**, 238-245 (2012)
- 6) Cao, J. P.; Li, L. Y.; Morishita, K.; Xiao, X. B.; Zhao, X. Y.; Wei, X. Y.; Takarada, T., *Fuel*, **104**, 1-6 (2013)
- 7) Xiao, X.; Meng, X.; Le, D. D.; Takarada, T., *Bioresour. Technol.*, **102**, 1975-1981 (2011)
- 8) Cao, J. P.; Xiao, X. B.; Zhang, S. Y.; Zhao, X. Y.; Sato, K.; Ogawa, Y.; Wei, X. Y.; Takarada, T., *Bioresour. Technol.*, **102**, 2009-2015 (2011)
- 9) Le, D. D.; Xiao, X.; Morishita, K.; Xianbin, X.; Takarada, T., *J. Chem. Eng. Jpn.*, **57**, 4251 (2009)
- 10) Nishiyama, Y.; Terada, K., *Kagaku Kougaku Ronbunshu*, **20**(1), 793 (1994)
- 11) Murakami, M.; Fuda, K.; Sugai, M., *J. of MMIJ*, **125**, 38-42 (2009)
- 12) Kishi, H.; Padama, A. A. B.; Areralo, R. L.; Moreno, J. L. V. *et al.*, *J. of Phys. Condens. Matter*, **24**, 262001 (2012)
- 13) Inada, Y.; Nomura, M., *Photon Factory News*, **23**, 1 May
- 14) White, B.; Yin, M.; Hall, A.; O'Brien, S. *et al.*, *Nano letters*, **6**(9), 2095-2098 (2006)
- 15) Wu, G.; Guan, N.; Li, L., *Catalysis Sci. & Tech.*, **1**, 601-608 (2011)