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

Atsushi YOSHINO, Hidenari HOnI, 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 [Cu(NH3)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℃, 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 Cu2O 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.

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 calorie. 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. 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...
produced by burning at low temperature around 200℃.

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℃, 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℃, 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 ℃, 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 ℃ /45 min, ramp2 500-815 ℃ /60 min, hold 815℃, 60 min based on JIS M8812 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)

Fig. 2 Effect of pH on Copper loading

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.
The mechanism of the ion exchange is presumed that carboxy groups in brown coal exchange the protons and complex cations, for example [Cu(NH₃)₄]²⁺ as below \(^{11}\).

\[
2\text{COOH} + [\text{Cu(NH₃)₄}]²⁺ \leftrightarrow \text{COO}^- [\text{Cu(NH₃)₄}]⁻ + 2\text{H}⁺ \quad \text{Eq. (1)}
\]

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 Cu(OH)₂ particles are precipitated. When pH is increased over 8.8, Cu(OH)₂; particles are dissolved again, then copper and ammonium complex ions such as tetraamminecopper(II) ion [Cu(NH₃)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 NH₃; 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, Cu(OH)₂ and Cu₂O spectra are identified by wave form separation. Therefore ion exchange is not only mechanism of the Copper loading, but also Cu(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
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 8.56 wt% is burnt at 815℃ 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 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℃ 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℃. In usual coal combustion, volatile matter is released and burnt at 400-600℃. So, it is considered that copper and nickel play a role of a catalyst of gasification and/or oxidation. It is

### Table 4 Repetition effect on Copper loading

<table>
<thead>
<tr>
<th>Item</th>
<th>1st time loading</th>
<th>2nd time loading</th>
<th>3rd time loading</th>
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<tbody>
<tr>
<td>Before Loading</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu content in ETS(Cl)</td>
<td>1.028</td>
<td>0.590</td>
<td>0.183</td>
</tr>
<tr>
<td>pH</td>
<td>9.60</td>
<td>9.54</td>
<td>8.95</td>
</tr>
<tr>
<td>Brown coal added[g]</td>
<td>5.05</td>
<td>5.04</td>
<td>5.07</td>
</tr>
<tr>
<td>After Loading</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-loading on Brown coal[g]</td>
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<td>0.407</td>
<td>0.152</td>
</tr>
<tr>
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<td>8.08</td>
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<td>0.031</td>
</tr>
<tr>
<td>pH</td>
<td>9.54</td>
<td>8.95</td>
<td>7.54</td>
</tr>
</tbody>
</table>
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 coal12) ~ 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,
\[ \text{COO-}[\text{Cu(NH}_3)_4]\text{-OOC \rightarrow Cu \rightarrow Cu}_2\text{O \rightarrow CuO} \quad \text{Eq. (2)} \]

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
SEM image of the residue taken at 180℃ 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 Cu₂O crystal.

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

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 [Cu(NH₃)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℃, and 0.5-1.0 μm copper oxide particles are formed as the residue.

Since XRD spectra of the sample taken at 165℃ shows Cu₂O, it is considered that Cu₂O 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