



Recovery of cupric oxide from copper-containing wastewater sludge by acid leaching and ammonia purification process

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ABSTRACT

The purpose of this study is to provide an efficient, simple, and economical method for the recovery of copper and removal of oil residue from copper-containing wastewater sludge using acid leaching and ammonia purification. In the first stage, sulfuric acid and hydrogen peroxide were used to leach a homogeneous suspension. The copper extraction percentage exceeded 90% in 30 min and oil residue was removed from the sludge. In the second stage, ammonia/ammonium carbonate media were used to purify the sulfuric acid leachate by forming an ammine complex. Through this process, ammonium hydroxide was recovered using an evaporating device and copper hydroxide was transformed into cupric oxide. The purity of copper in the oxide compound reached 98.26%. The economic evaluation of this process for a capacity of six tons of copper-containing wastewater sludge per day is discussed. For an initial capital investment of NT\$3.2 million with annual operating and maintenance costs of about NT\$3.13 million, the comparative savings in sludge treatment would be about NT\$1.44 million per year. Given an annual net profit from sales of cupric oxide powder of about NT\$3 million, total investment in the two-stage leaching process would be repaid in 30 months.

Keywords: Copper-containing wastewater sludge; Acid leaching; Ammonia leaching; Cupric oxide

1. Introduction

Electroplating, surface finishing, and coating industries generate a large amount of wastewater containing various heavy metals [1,2]. In Taiwan, such wastewater is typically treated using chemical precipitations. Polyvalent metal ions (e.g. Al³⁺, Fe²⁺, and Fe³⁺) are generally used because they are hydrolyzed

in water to form polynuclear complexes. Initial wastewater treatment generally involves coagulation–flocculation followed by sedimentation. The coagulating agents used in the treatment of wastewater and heavy metal contaminants in sludge likely produce aluminum or ferric salts depending on the types of coagulants used [2]. Metal plating has been identified as an environmentally risky industrial sector due to the potentially hazardous nature of its waste streams with industrial sludge which typically contains

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residues of Al, Fe, Cu, Ni, Zn, Cr, and Mn. Sludge from the surface finishing industry does not meet the regulation standards and is classified as hazardous industrial waste according to the Standards for defining hazardous industrial waste [3]. Such waste must be treated carefully, including stabilization/solidification procedures at high cost, before landfill disposal. Heavy metal contaminated sludge presents a heavy social, legal, and financial burden (up to NT\$12,000 per ton) to the electroplating and surface finishing industries. The recovery of valuable metals and efficient, effective neutralization of contaminated sludge is of great interest to governments and industry. To this end, a number of technical feasibility studies focusing on waste (sludge) minimization and resource recovery have been conducted [4–6]. In order to reduce environmental damage and recover valuable metals for industrial reuse, various hydrometallurgical technologies have been developed to enable the treatment of industrial sludge.

Sulfuric acid and ammonia are generally used to leach out copper minerals. In fact, for copper-containing wastewater sludge, the cost of acid may be the most important economic factor [7,8]. Acid leaching has been used to recover metals such as Cu, Ni, Zn, Cr, and Cd from inorganic wastes. The main advantages of alkaline leaching over acid leaching are improved selectivity, less corrosiveness, and lower reagent consumption for calcareous carbonate gangue. The important parameters in ammonia leaching of malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) ore are leaching time, ammonia/ammonium concentration ratio, pH, solid/liquid ratio, leaching temperature, and particle size [9]. Ammonium hydroxide is commonly used in Co, Ni, and Cu industries due to the formation of stable metal amine complexes. Compared to acid leaching, however, alkaline leaching is less efficient in metal extraction.

According to Taiwan's EPA and Industrial Development Bureau (2006), the copper-containing wastewater sludge produced in Taiwan from the manufacturers of printed circuit boards, electroplating, and surface finishing is estimated to be 146,000 tons per year [10]. This means there is a grave need for efficient, economically viable, environmental friendly sludge treatment and disposal. In recent years, there has been much interest in cupric oxide (CuO) whiskers for their remarkable optical, electrical, magnetic, and mechanical properties [11]. The direct recovery of CuO from copper-containing wastewater is difficult and uneconomical. The hazardous heavy metal sludges were the final residues from the wastewater treatment process. Thus, the recovery of copper and removal of oil residue from copper-containing wastewater sludge (40 tons/month and 78% of water

content) using acid leaching and ammonia purification is an efficient, simple, and economical method that not only solves the problem of storage of hazardous heavy metal sludge, but may also lead to more valuable product for the use of recycled resources.

One difficulty in the development of realistic alternatives for the salvaging of valuable metals from industrial sludge in Taiwan is the size of the contributing enterprises, which are generally small- to medium-sized businesses (small-medium enterprises). Therefore, this study provides an efficient method for selectively dissolving metals from copper-containing wastewater sludge. The method proposed is simple, eco-friendly, and economically viable for the removal of oil residue from the sludge and recovery of copper, ammonium hydroxide, and leachate from cupric oxide solution. The study also looks at the economic viability of potential wastewater sludge treatment plants to see if they would be attractive to small-medium enterprises. The recovery process follows a two-stage procedure. Stage I includes homogenization at a liquid to solid ratio of 5 and sulfuric acid and hydrogen peroxide being poured over the suspension to form a leachate that contains copper and other metals extracted from the sludge. In Stage II, metallic hydroxides, other than copper hydroxide, are produced in an ammine solution that is formed by adding ammonia/ammonium carbonate media to the leachate. The ammine solution is heated to an appropriate temperature and the pH adjusted to first remove and recover ammonium hydroxide and leachate from the solution of cupric oxide, after which cupric oxide crystals are precipitated. This transformation of copper hydroxide to cupric oxide is analyzed using X-ray diffractometer (XRD) and scanning electron microscope (SEM) to examine the crystal phase of the sediment. Ultimately, high purity cupric oxide powder is recovered [4,12–16]. Thus, the aim of this study is to investigate and discuss the feasibility of recycling plants for the recovery of valuable material from copper-containing wastewater sludge by the two-stage leaching process.

2. Materials and method

2.1. Copper-containing wastewater sludge

The sludge sample was collected from the manufacturers of copper wire and anodes at Yong-Kang Industrial Park in Tainan. The heavy metals contaminated wastewater had been treated in a plant using a chemical precipitation process (PAC, polyaluminum chloride) with a capacity of 300 m³/day. Table 1 shows the wastewater characteristics in the copper

Table 1
Characteristics of wastewater from copper wire and anodes industries

Items	Unit	High copper-containing wastewater	General wastewater	Effluent	Effluent standards
pH	–	2.0	2.3	7.1	6.0–9.0
Temp.	°C	25.6	26.1	26.9	<38.0
COD	mg/L	408	75.6	15.5	100
SS	mg/L	916	7.7	1.7	30
Oil	mg/L	1.4	1.7	0.3	10.0
Cr	mg/L	0.03	N.D.*	<0.01	2.0
Cu	mg/L	305	29.3	0.37	3.0
Ni	mg/L	0.05	0.01	<0.01	1.0
Pb	mg/L	0.21	0.02	N.D.	1.0
Zn	mg/L	0.12	0.03	<0.01	5.0
As	mg/L	N.D.	N.D.	N.D.	0.5
Cr ⁺⁶	mg/L	N.D.	N.D.	N.D.	0.5
CN [–]	mg/L	N.D.	N.D.	N.D.	1.0

Note: N.D.: Below the detection limit.

wire and anodes industries. The chemical oxygen demand (COD), suspended solids (SS), and copper content were higher than the effluent standards. Additionally, around 40 tons/month of copper-containing wastewater sludge was discharged from the wastewater treatment system (Fig. 1). The treatment cost of hazardous waste was about 8,000–12,000 NTD per ton. Thus, the recovery CuO from hazardous wastewater sludge into a valuable resource have become key focus points in the wastewater treatment technological development. The sludge was characterized by its composition and pH value. During the experiments, the sample was dried and processed using industrial grade chemicals.

2.2. Analytical methods

Metals were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES) on a VARIAN VISTA-MPX ICP-OES spectrometer. An XRD (Bruker AXS-D8) was used to examine and scan the crystalline phases of products in purification experiments from 10 to 80° (2θ) at a scan rate of 4°/min. In SEM (Hitachi 3000) analysis, a small amount of CuO powder was dispersed in ethyl alcohol and shaken in an ultrasonic machine for 10 min. Qualitative analyses were carried out using a SPECTRO Instruments XEPOS X-ray fluorescence spectrometer.

2.3. First-stage leaching: selective acid leaching

During this stage, the sludge was homogenized and subjected to sulfuric acid leaching and hydrogen peroxide oxidation. Firstly, the wet base of the

copper-containing wastewater sludge after filter pressing (1,000 g) was stirred in 5,000 ml of hot water at a liquid to solid ratio of 5 for 0.5 h at 400 rpm to form a homogeneous suspension. The most important parameters affecting the leaching were time, acid concentration, stirring speed, and temperature of the medium. Leaching was found to comprise two steps, namely an initial, very rapid dissolution of about 85% copper recovery within 15 min and a gradual second step. An amount of 220 ml of 60 wt.% sulfuric acid (H₂SO₄) and an amount of 100 ml of 30 wt.% hydrogen peroxide (H₂O₂) reagents were added to the suspension, with optimal conditions as follows: reaction temperature of 80°C, reaction time of 1 h, stirring rate of 400 rpm; sulfuric acid and hydrogen peroxide reagents were finally added to control the pH below 3. At the end of this reaction, the suspension was filtered.

2.4. Second-stage leaching: ammonia purification

The sulfuric acid leachate purification experiment was carried out by precipitation, ammonia evaporation, and oxidation. Ammonia (30 wt.% NH₄OH)/ammonium carbonate ((NH₄)₂CO₃) agents were added to sulfuric acid leachate to adjust the pH to 9–10 and form a stable Cu-ammine (Cu(NH₃)₄²⁺) complex and metallic hydroxide. After filtration, the ammine solution was heated to remove and recover ammonia, in which crystalline copper hydroxide had formed, from the solution. The suspension was then heated to 80°C. At this temperature, using an aeration rate of 5 ml air/min and 400 rpm stirring speed, the alkali agent (sodium hydroxide, NaOH) was added to the suspension and a pH value close to 11 was achieved in 3 h,

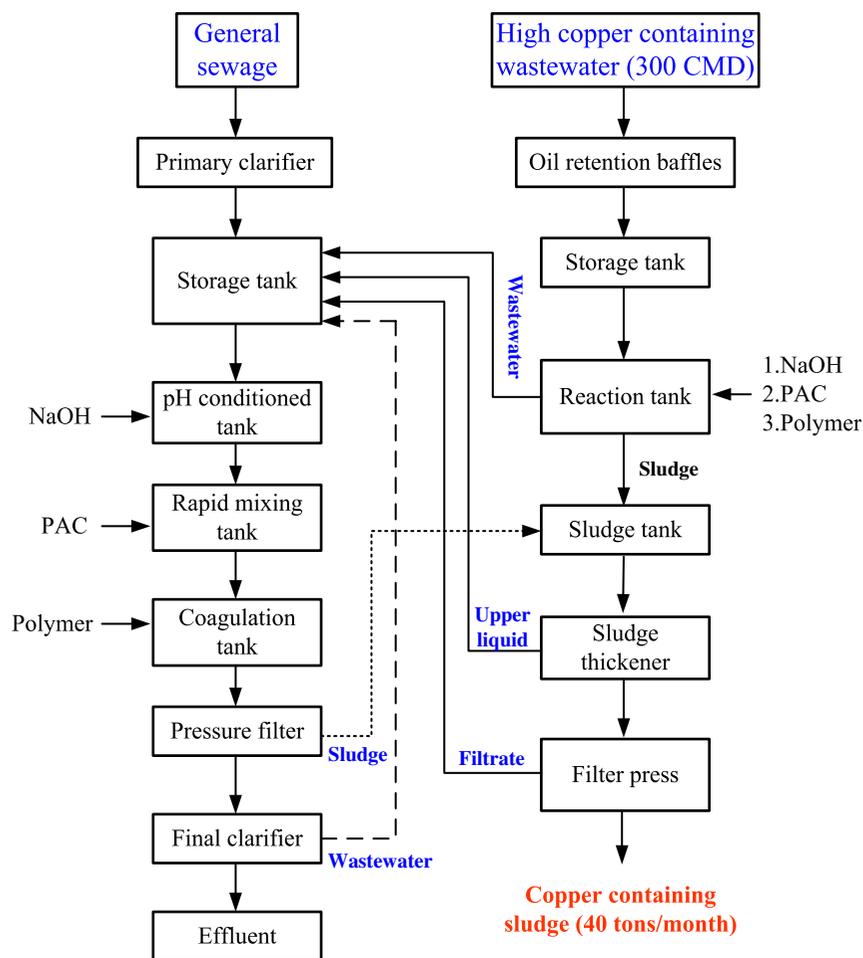


Fig. 1. The wastewater treatment process of copper wire and anodes industries.

after which cupric oxide crystals were precipitated. One of the advantages of this method is recovery of ammonium hydroxide (NH_4OH) and leachate from the solution of cupric oxide. The structure of the final black product was characterized by XRD, SEM imaging, and TEM and quantitatively analyzed by ICP-OES and X-ray fluorescence (XRF). A flowchart of the overall treatment process is shown in Fig. 2.

3. Results and discussion

3.1. Characteristics of copper-containing wastewater sludge

The fundamental properties and composition of the copper-containing wastewater sludge are given in Table 2. The water, ash, and flammable content of the sludge gave weight percentages of 78.0, 11.4, and 10.6%, respectively. The moisture content of the sludge after filter pressing was too high for direct use. A weight percentage of 10.6% for the flammable component indicates a high level of organics from cutting oil, lubricants, and emulsifier that are used

in copper wire and anode production. The weight percentage of copper in the dried sludge was 17.35%. The copper content in the dried sludge was higher than 0.4%, which is the mining grade for copper ore. The other minor metal weight percentages were Al: 10.46% and Ca: 1.48%. Trace elements such as Na, Zn, Pb, and Ni were lower than 0.4%. The toxicity characteristic leaching procedure (TCLP) results show that only the leaching of Cu is higher than the Standards for defining hazardous industrial waste (15 mg/L). The SEM/energy-dispersive spectrum (EDS) analysis of copper-containing wastewater sludge is shown in Fig. 3. The SEM/EDS result also indicates copper-containing wastewater sludge contents are mainly copper, aluminum, and magnesium.

3.2. Two-stage leaching process and recovery of cupric oxide

In the acid leaching and oxidization processes, 220 ml of 60 wt.% sulfuric acid (H_2SO_4) and 100 ml

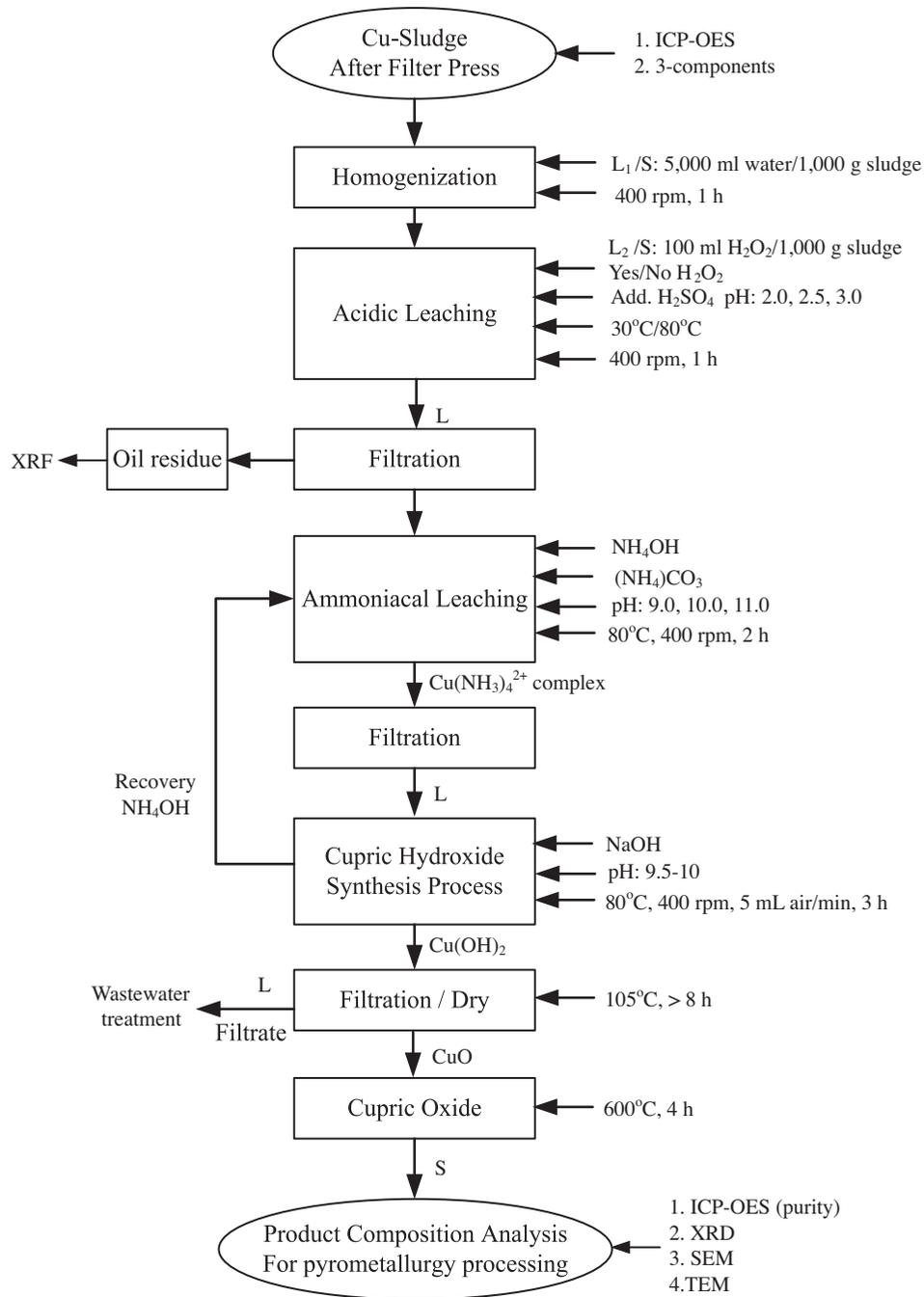


Fig. 2. Flowchart of overall treatment process.

Table 2
Characteristics and compositions of copper-containing wastewater sludge

pH	Three components (%)			Total concentration (mg/kg)								TCLP (mg/L)	
	Water	Ash	Inflammable	Al	Cu	Ca	Fe	Na	Ni	Pb	Zn	Cu	Pb
8.31	78.0	11.4	10.6	104,555	173,570	14,761	2,934	3,924	18	57	133	279	2.3

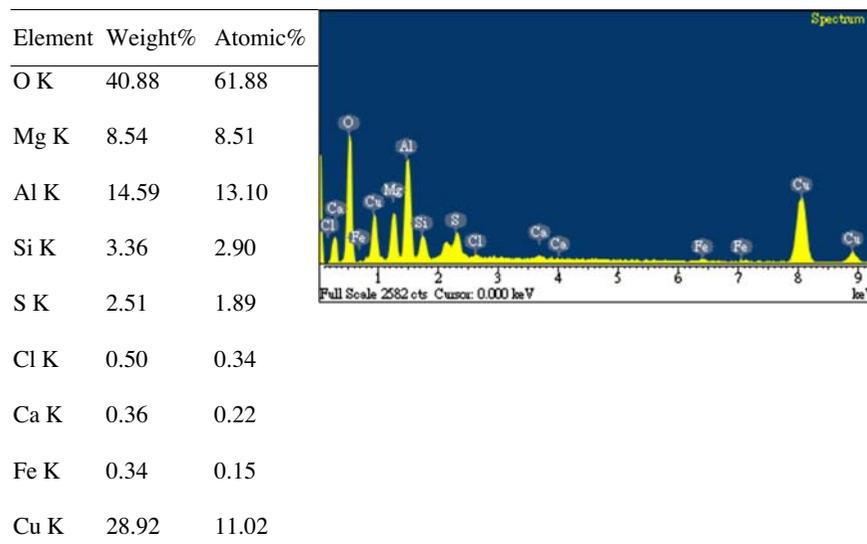
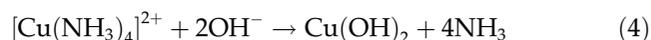
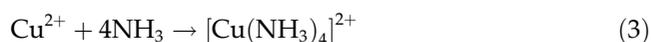
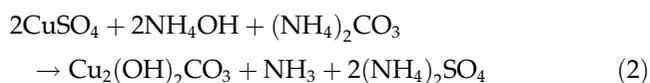


Fig. 3. SEM/EDS analysis of copper-containing wastewater sludge.

of 30 wt.% hydrogen peroxide (H_2O_2) reagents were added to the suspension, and the pH value of the leachate was found to be 2.87. At this stage, a great deal of oil residue could be gravity filtered and removed from the suspension. In the second stage, ammonia was used as complexation reagent to neutralize the product of the first-stage acid leaching. It is known that ammonium carbonate plays an important role in buffering the leaching solution, thus preventing pH to rise to the point where Ni and Cu can precipitate as their hydroxides ($\text{pH} > 10$). Furthermore, NH_4^+ ions, supplied by the ammonium salt, can improve the occurrence of amine complex reactions by removing OH^- ions. Consequently, a critical compromise between ionic strength and pH is needed to enhance the leaching efficiency of ammonia in the copper-contaminated wastewater sludge. The region where $\text{Cu}(\text{NH}_3)_4^{2+}$ complex is stable is defined as a function of temperature, total ammonia concentration $[\text{NH}_3] + [\text{NH}_4^+]$, and pH. The optimum pH range for stable copper complex is between 8.3 and 10.8.

The total chemical reactions that are involved in the growth of CuO powder in suspension are thought to proceed as follows:



According to the Eh-pH diagram and thermodynamics of the Cu-H-O system, copper hydroxide in the system is transformed into stable copper oxide at a higher pH value [17]. Because the decrease in pH value of the alkaline solution during the aeration period resulted in the formation of $\text{Cu}_4\text{SO}_4(\text{OH})_6$, the pH value of the solution had to be adjusted to a value near 11 to prevent a decrease in pH to 10 [18]. When the oxide reaction was completed, the copper hydroxide was transformed to copper oxide, of which the XRD pattern is depicted in Fig. 4. The XRF results of the preliminary characterization of the oil residue are shown in Table 3. The major elements were Al, Si, Ca and Fe. The oil residue with 30% H_2O_2 would enhance the recovery of copper oxide.

The recovery percentage of copper from the ammine solution ranged from 90.6 to 95.6% (Table 4). In the cupric oxide synthesis process, copper hydroxide was transformed into copper oxide. The copper concentration reached 78.5% at the best reaction condition, which is more than the copper purity required for commercial CuO powder (78.2%). The CuO purity of the product recovered from the purification experiment was 98.3%, which is also more than the purity of commercial product requirements of CuO powder

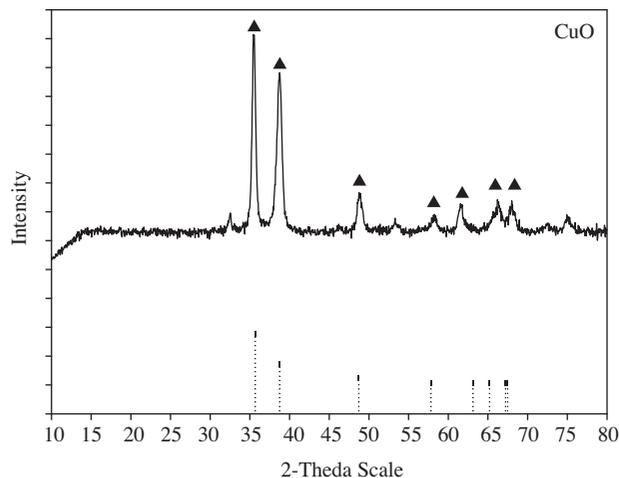


Fig. 4. XRD pattern of the recovered product.

Table 3
The XRF result of the oil residue (%)

Main element	Al	Si	Ca	Na	Fe
Without 30% H ₂ O ₂	6.25	2.45	0.65	0.14	0.10
With 30% H ₂ O ₂	7.31	2.68	0.73	0.18	0.09

Note: Condition: pH 2.0 and 80°C.

(97.89%). The levels of the other trace impurities in the recovered product, such as Cl, Ca, Fe, Ni, Pb, Zn, Sn, Cr, Cd, and Hg, were 8, 14, 42, 16, 24, 43, 2, 35, 0.8, and 0.3 mg/L, respectively (Table 5). The purity of the CuO product meets the criteria of commercial CuO powder. The dissolving time of the recovered product was 60 s, which is within the standard required for commercial CuO powder (90 s). Table 5 shows the difference between commercial CuO powder and the recovered high purity CuO powder of these experiments. In most countries, copper metallurgy requires a copper content of >25%. These experiments improved the content of copper in dried sludge from 17.36 to 78.5%.

3.3. XRD, SEM, and TEM analysis of recovered CuO product

The crystal phase of the recovered CuO product was determined by XRD analysis, and the XRD pattern is shown in Fig. 4. It shows that the XRD pattern of the recovered sample corresponds to that of monoclinic CuO (Tenorite, syn) crystal with lattice constants of $a=0.4684$ nm, $b=0.3425$ nm, $c=0.5129$ nm, and $\beta=99.47^\circ$ (JCPDS card No. 05-0661).

Fig. 5 shows the SEM image of the recovered CuO powder. It can be clearly observed that the CuO has a belt or roll structure composed on average at 150–350 nm in width and 200–400 nm in length. This indicates that the CuO was piled together intensely with many tiny particles. The EDS further proves that the recovered CuO is composed of Cu and O elements.

The TEM image of the recovered CuO powder is shown in Fig. 6. The recovered CuO product exhibits a feather-like structure with average 200–400 nm in length. The feather-like structure consists of several narrow nanosheets or fine nanorods similar to that of the previous study [11]. When comparing the first and second highest diffraction peaks of the recovered CuO with those of monoclinic CuO, the recovered CuO also shows the existence of CuO nanorods.

3.4. Economical evaluation

Table 6 gives the preliminary economical estimation for a copper recovery plant. The copper contaminated sludge is treated by the two-stage leaching procedure at a capacity of six tons per day. The economically significant parameters such as construction costs and operating and maintenance expenses are also considered. Using most probable values as an estimate, the costs of wastewater treatment in the manufacturers of copper wire and anode industry are NT\$2.48 million per year. If a recovery plant was to adopt the two-stage leaching process, the cost of wastewater treatment could be decreased greatly. For the two-stage process with a capacity of six tons per day, the capital cost would be NT\$3.2 million. Annual operating and maintenance costs would be about NT\$3.13 million. Annual saving of hazardous industrial waste treatment would be about NT\$1.44 million. Annual net profit from the high purity cupric oxide powder produced would be about NT\$3 million. Consequently, an investment using this two-stage leaching process could be returned in 30 months.

The economical evaluation shows that the treatment process can compete with conventional processes due to low treatment costs, recovery of valuable materials, and high revenue returns.

4. Conclusion

The overall recovery of metallic species and the difficulty of their separation from other undesirable metals are generally governed by the efficiency and selectivity of the leaching process. A two-stage procedure was proposed and tested. In the first stage, homogenization was undertaken with sulfuric acid

Table 4
Recovery of copper after acid leaching and ammonia purification process

Acidic leaching		Ammoniacal leaching	Recovery % of copper (%)	Purity of copper (%)	Copper oxide (%)
Temp.	pH	pH			
30	2.0	9.0	93.2	77.1	96.5
	2.5	9.0	92.5	76.8	96.1
	3.0	9.0	90.8	76.6	95.9
	2.0	10.0	93.3	77.4	96.9
	2.5	10.0	92.7	77.4	96.9
	3.0	10.0	91.6	77.1	96.5
	2.0	11.0	91.8	77.3	96.8
	2.5	11.0	91.3	77.4	96.9
	3.0	11.0	90.6	77.3	96.7
80	2.0	9.0	95.1	78.5	98.2
	2.5	9.0	93.8	78.4	98.2
	3.0	9.0	92.5	78.2	97.8
	2.0	10.0	91.3	77.5	97.0
	2.0	10.0*	95.6	78.5	98.3
	2.5	10.0	95.4	78.6	98.3
	3.0	10.0	93.9	78.4	98.2
	2.0	11.0	91.0	78.3	98.0
	2.5	11.0	90.5	78.2	97.9
3.0	11.0	90.9	78.1	97.7	

Notes: Condition:

1. Acidic leaching: 2 N H₂SO₄, 400 rpm, and 1 h;

2. Ammoniacal leaching: 5 N NH₄OH, 0.2 M (NH₄)₂CO₃, 80 °C, 400 rpm, and 2 h.

*With 30% H₂O₂ (100 ml 30% H₂O₂: 1,000 g sludge).

Table 5
Difference between commercial CuO powder and the recovered CuO powder

Standards		Commercial CuO powder	Recovered CuO powder*
Purity	Cu (%)	>78.2	78.5
	CuO (%)	>97.89	98.26
Impurity	Cl (mg/L)	<30	8
	Ca (mg/L)	<60	14
	Fe (mg/L)	<60	42
	Ni (mg/L)	<60	16
	Pb (mg/L)	<60	24
	Zn (mg/L)	<60	43
	Sn (mg/L)	<30	2
	Cr (mg/L)**	<1,000	35
	Cd (mg/L)**	<100	0.8
	Hg (mg/L)**	<1,000	0.3
Dissolving time (Sec.)		<90	60

Notes: *Condition:

1. Acidic leaching: 2 N H₂SO₄, 80 °C, 30% H₂O₂, 400 rpm, and 1 h;

2. Ammoniacal leaching: 5 N NH₄OH, 0.2 M (NH₄)₂CO₃, 80 °C, 400 rpm, and 2 h.

**ROHS standard.

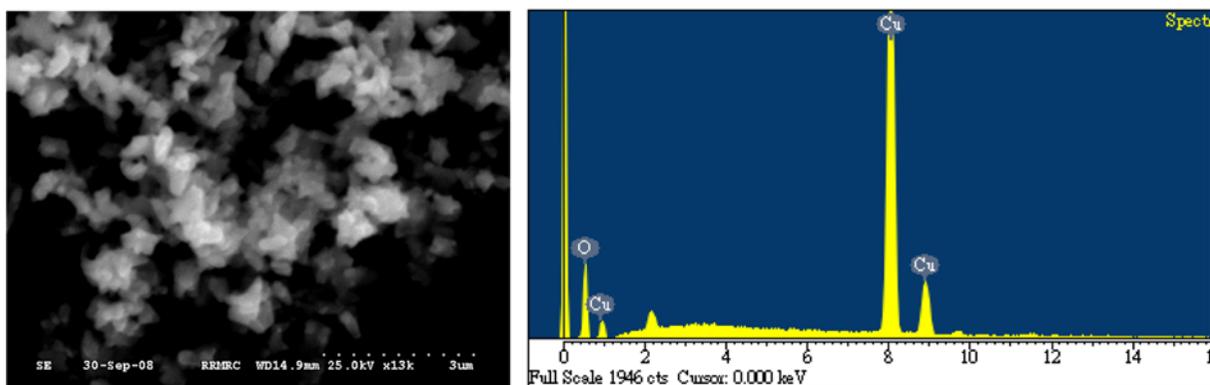


Fig. 5. SEM image of the recovered CuO powder.

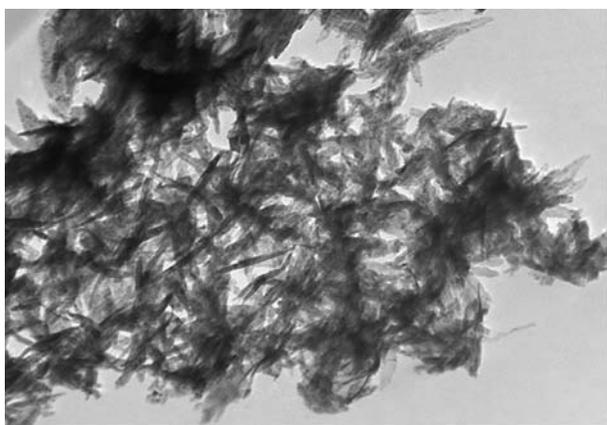


Fig. 6. TEM images of the recovered CuO powder.

Table 6
Economical estimation for a copper recovery treatment plant by the two-stage leaching process

Item	Cost (NTD\$)
(1) Capital cost of Cu recovery plant	3,200,000
(2) Maintenance and operating cost per month	260,500
(3) Treatment saving fee of sludge of hazardous industrial waste clearance and disposal per month	120,000
(4) Net profit of CuO powder products per month	250,000
(5) Net profit per month (5) = (4) + (3) – (1) – (2)	109,500
(6) Period of return (5) = (1)/(4) (month)	29.2

and hydrogen peroxide reagents being added to leach the homogeneous suspension. Optimal conditions were a reaction temperature of 80 °C, stirring rate of

400 rpm, and pH below 3. In the second stage, ammonia/ammonium carbonate media were used to purify the sulfuric acid leachate by forming an ammine complex. The CuO purity of the product recovered from the purification experiment was 98.26%. This level of purity meets the criteria of commercial CuO powder (97.89%). The study provides discussion on the future of cupric oxide whiskers as miniature circuits as they exhibit remarkable optical, electrical, magnetic, and mechanical properties. In addition, the economic feasibility of processing six tons of copper-containing wastewater sludge is examined and found to be viable. The capital cost would be NT\$3.2 million. Annual operating and maintenance costs would be about NT \$3.13 million. Annual saving of hazardous industrial waste treatment and net profit of cupric oxide powder product would amount to about NT\$4.44 million. Therefore, the total investment in a two-stage leaching process could be paid back in 30 months.

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References

- [1] A. Agrawal, K.K. Sahu, An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, *J. Hazard. Mater.* 171 (2009) 61–75.
- [2] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage.* 92 (2011) 407–418.
- [3] M.C. Huang, J.J. Lin, Characteristics and management of infectious industrial waste in Taiwan, *Waste Manage.* 28 (2008) 2220–2228.
- [4] K. Fytianos, E. Charantoni, Leaching of heavy metals from municipal sewage sludge, *Environ. Int.* 24 (1998) 467–475.
- [5] C.W. Li, J.L. Lin, S.F. Kang, C.L. Liang, Acidification and alkalization of textile chemical sludge: volume/solid reduction, dewaterability, and Al(III)recovery, *Sep. Purif. Technol.* 42 (2005) 31–37.

- [6] P. Prakash, A.K. Sengupta, Selective coagulant recovery from water treatment plant residuals using Donnan membrane process, *Environ. Sci. Technol.* 37 (2003) 4468–4474.
- [7] D.H. Rubisov, V.G. Papangelakis, Sulphuric acid pressure leaching of laterites—speciation and prediction of metal solubilities “at temperature”, *Hydrometallurgy* 58 (2000) 13–26.
- [8] N.M. Al-Mansi, N.M. Aabdel Monem, Recovery of nickel oxide from spent catalyst, *Waste Manage.* 22 (2002) 85–90.
- [9] D. Bingol, M. Canbazoglu, S. Aydogan, Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching, *Hydrometallurgy* 76 (2005) 55–62.
- [10] S.H. Hu, The study of resource recovery from metal-contaminated sludge produced in the manufacturing procedure of printed circuit board, Ph.D. thesis, National Cheng Kung University, Tainan, Taiwan, 2006.
- [11] H. Zhang, M. Zhang, Synthesis of CuO nanocrystalline and their application as electrode materials for capacitors, *Mater. Chem. Phys.* 108 (2008) 184–187.
- [12] S.H. Hu, J.Y. Wu, F.S. Yen, M.S. Tsai, Alkaline leaching of printed circuit board sludge, *Environ. Prog.* 25 (2006) 243–250.
- [13] S.H. Hu, M.S. Tsai, F.S. Yen, T. Onlin, Recovery of copper-containing sludge in a two stage leaching process, *Environ. Prog.* 25 (2006) 72–78.
- [14] D. Bingol, M. Canbazoglu, Dissolution kinetics of malachite in sulphuric acid, *Hydrometallurgy* 72 (2004) 159–165.
- [15] J.E. Silva, D. Soares, A.P. Paiva, J.A. Labrincha, F. Castro, Leaching behaviour of a galvanic sludge in sulphuric acid and ammonia media, *J. Hazard. Mater.* 121 (2005) 195–202.
- [16] N. Sato, T. Okubo, T. Onodera, L.K. Agrawal, A. Ohashi, H. Harada, Economic evaluation of sewage treatment processes in India, *J. Environ. Manage.* 84 (2007) 447–460.
- [17] S.H. Hu, M.S. Tsai and T. Onlin, The study on resource recovery of sludge containing heavy metals and its residue stabilization. Proceedings of the 6th International Symposium on East Asian Resources Recycling Technology Conference, Kyongju, Korea (2001) 448–452.
- [18] H. Tanaka, M. Kawano, N. Koga, Thermogravimetry of basic copper(II) sulphates obtained by titrating NaOH solution with CuSO_4 solution, *Thermochim. Acta* 182 (1991) 281–292.