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The Study on Resource Recovery of Sludge Containing Heavy Metals and its Residue Stabilization

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An experimental study was carried out to develop a simple method of processing copper waste sludge which is produced by PBC manufacturing. The procedure is based on leaching of wet sludge in 2N H_2SO_4, and the solid / liquid ratio is controlled approximately at 1/10. The recovery of copper is 85.4%, and pH of the leachate is 3.20. Adding ammonia solution into leachate forms ammine, and hydroxide compounds derived from other impurities in leachate at pH 10. The hydroxide compound can be treated by ferrite process, and the product is a stable oxide compound. Then the ammine solution is heated to evaporate ammonia, and the copper hydroxide is formed. Heating at 80^0 C by aeration, copper hydroxide is transformed into copper oxide with a purity of 98.4%. This process can recover most copper from sludge and the residue can be stabilized by the formation of a stable oxide compound which is not hazardous to environment.
Keywords: recovery, ammine, stabilization.

Introduction

Due to the fast expansion of electronics, printed circuit board (PCB) and communication industry, the waste sludge produced in these industry lead to severe environmental pollution. The pollutants were produced mainly from waste etching solution and waste washing water in the process. Neutralization and precipitation with lime is the most widely used treatment process in the electronics industry. Mixing the pollutants together resulted in increasing complex of resource recovery. The resulting sludge contains hydroxide of heavy metals and different amount of moisture. The sludge is transported and disposed by special waste disposal agent. However, the great quantity of sludge represents a raw material for the recovery of heavy metal, such as copper. The concentration of copper ranges from 1.2% to 40% in the dry sludge, but most samples contains about 20% copper in this research (sample A, B C).

The sludge tested by TCLP procedure reveals that the extraction values of copper and lead are 76~350mg/l and 0~0.8 mg/l respectively [1]. On the other hand, the wet sludge (moisture 85%) quantity estimated to be 120,000 tons every year in Taiwan [1]. In proportion to the demand of copper foil is very large quantity in PCB manufacturing. Due to the reason, there are about six large scale factories to produce copper foil and supply it for PCB manufacturing in Taiwan. It is similar of the contaminated copper sludge (sample D and E) produced in waste water treatment. It is estimated that have 326 production lines, and the sludge is produced about 29,340 tons every year. The character of the sludge is list in table 1, and it is obvious copper composition is higher than the other kind of sludge. But the sludge contains great quantity of nickel, so it is not adequate for the treatment in this research. And it will be a subject in next research.

Assuming the weight percent in sludge of copper is 20% (dry base) and the price of refined copper is 3,692 NT dollars /ton [2], the potential value of copper recovery is 13,291,200 NT dollars. In order to reduce environmental damage and recover heavy metal for industrial re-use, various hydrometallurgical technologies have been developed to enable the treatment of the sludge. These technologies are frequently based on combinations of relatively expensive and difficult methods such as liquid-liquid extraction, ion exchange, and electrochemical separation [3~4]. However, due to high investment and operation cost, particular attention is focused on developing specific methods suitable for copper recovery from relatively simple and defined mixture.

The object of this research is to develop a simple method to recover copper from contaminated sludge and stabilize its residue. The operation procedure is based on acid leaching of sludge, and precipitates metals hydroxide except copper ion by adding ammonia solution. Then a great majority of copper will be separated from other metals hydroxide. The copper (II) ammine solution is treated under proper temperature and pH value at next step to remove ammonia from solution and form copper hydroxide. The filtrate contains some impurity ions such as manganese, aluminum, and calcium etc. After crystallizing, a great majority of copper hydroxides were produced. Meanwhile the impurity was hold in filtrate by keeping the pH value close to 10. According to Eh-pH diagram, the copper hydroxide system will form stable copper oxide at high pH. [5].The conditions of aeration hydrolysis were investigated and the product were analyzed with XRD and XRF to observe crystal phase and composition.

On the other hand, when the copper (II) ammine solution is formed, the metals hydroxide and a part of copper species are formed in the residue. The residue thus may be hazardous to the environment and must be treated further. The ferrite process is utilized to synthesize ferrite (MFe_2O_4) by air oxidation of the metal hydroxide in aqueous suspensions. Metal ions in solution are eliminated by combining into spinel structure [6]. The oxide structure is stable enough to prevent the metal ions dissolved out again in the solution [7].

The resource recovery procedure used in this study can recover a great majority of copper oxide from waste sludge and stabilize its residue to avoid polluting again.

Experiment

Sludge samples were obtained from the waste water treatment plant of PCB manufacturing. In order to realize its hazard to the environment, the sludge was checked by EPA TCLP procedure. XRF (Rigaku) and XRD (Rigaku) were used to check the composition and crystal phase of sludge. The beam splitting crystals of XRF analysis are LiF and EDDT. And the XRD spectroscopy was scanned from 10^0 to 80^0 (2θ) with a scan rate of 4^0 min^{-1}.

Leaching experiment using sulfuric acid was performed to realize the leaching behavior of copper from the sludge. Fifty gram of wet sample A was mixed with 100 ml sulfuric acid in a vessel. The ratio of dry solid weight and sulfuric acid volume was controlled approximately at 1:10. The vessel was placed for 12 hr and then stirred 1 hr at 500 rpm. And finally the leachate is collected in a 250ml vessel. The metals in filtrate were analyzed by atomic absorption spectrum (GBC, model 932). Copper was analyzed by UV (HP, model 8453).

The next experiment was leachate purification by precipitation, evaporation and aeration oxidation. Ammonia solution (29% wt%, Acros) was added 100ml leachate to adjust pH into 10 to form ammine solution and metals hydroxide. After filtrating, the ammine solution was heated on hot plate to remove ammonia from the solution, and the crystalline copper hydroxide was formed. Copper hydroxide was put in vessel and aerated twice to form copper oxide. This product can be identified by X-ray diffraction. The reaction conditions were as followed: reaction temperature was 80^0C, aeration rate was 3 liter /min, first stage pH of the liquor was adjusted to 12.0, second stage pH was adjusted to 12.7, and reaction time was all about 3 hr.

Residue stabilization was achieved by using the ferrite process to form stable oxide compound. The operation conditions were as followed: liquor volume was 500 ml, $Fe(OH)_2$=0.25M, aeration rate was 3 liter/min, pH of the liquor was adjusted to 12.8, reaction temperature was 80^0, and reaction time was about 5 hr.

Results and Discussion

Characterization of the sludge

Sludge samples were obtained from PCB manufacturing (sample A, B, and C) and copper foil factories (sample D and E). The XRF result is showed in Fig. 1 (sample A). The primary constitute elements of sample A are copper, manganese, calcium, and aluminum (not show in XRF diagram). The crystal structure of sludge was analyzed by XRD. and peaks display armorphous types. This phenomenon may be caused by the influence of flocculant which was used in waste water treatment.

The fundamental properties and composition of sludge was analyzed, and the results shown in table 1. It reveals that the samples of sludge are possessed of high moisture, adequate pH except one sample (not show in table 1), and the quantity of copper in sludge vary from 1.2% to 44.0%. The high copper content may be hazardous to environment. So the sludge must be tested by TCLP procedure. The results of TCLP test for samples A ~ E were shown in table 2. The concentrations of copper in extract all exceed limitation. It reveals that copper will dissolved out of most samples and may be dangerous to environment. So the waste sludge must be proper treated before being buried in the landfill.

Leaching experiment

The sludge of sample A was leached with 0.1N ~ 4.0N sulfuric acid, and the ratio of solid weight of sludge to sulfuric acid volume is controlled at approximately 1:10. The data of copper recovery was shown in Fig. 2 Fig. reveals that near 100% of copper recovery was achieved by using 4.0 N sulfuric acid. The final pH of leachate is 0.31. The elemental composition of leachate leached by different concentration of sulfuric acid was shown in table 3. The concentration of lead, zinc, iron, manganese, and tin in leachate increases with increasing the concentration of sulfuric acid. For the purpose of keeping minimum impurity leach out and adequate pH of the leachate, 2N sulfuric acid was adopted to treat sample A at the next step. The final leachate pH value is 3.20 and the recovery of copper is 85.4%. This result is favorable for ammonia precipitation operation follow-up, and the residue can be recycle to be leached by counter current method. The sludge is leached by 2N sulfuric acid at first, residue then be delivered in the reverse direction with higher concentration sulfuric acid. At the same time, the acid concentration of leachate will decrease and use it in next leaching operation. Therefore the copper will be leached out completely from sludge.

Precipitation by ammonia solution experiment

For the purpose of seeking the optimum quantity of ammonia solution added to effectively decrease the impurity in the ammine. The leachate was used to realize the quantity of impurity in ammine solution after precipitation. Adding different quantity of ammonia solution to 100 ml eachate produce various precipitate. The composition of heavy metals in ammine solution was analyzed, and the result was shown in table 4. It is appearant that the concentration of copper increases with increasing pH. Other impurities were precipitated as metal hydroxide. It reveals that the tendence for forming ammine solution depends on pH since the speciation of ammonia in aqueous solution is determined by pH. When pH is adjusted to 10, copper recovery is about 91.2% and impurities except zinc are all severely decrease. Acknowledged that the acidity constant (k_a) of NH_4^+ equal to $10^{-9.3}$, the major species is NH_4^+ when pH is lower than 9.3 [8]. This can explain why the concentration of copper in ammine solution is higher at pH=10. The complex compound of copper (II) can occur only with NH_3, not with NH_4^+.

Crystallize and purify experiment of leachate

The copper complex compound is stable in ammine solution. For recycling of copper, ammonia must be stripped. The ammine solution was evaporated on hot plate to remove ammonia, and the ammonia gas can be collected for recovery. When evaporation proceeded, the crystalline copper hydroxide gradually produced, and the color of solution was pale. Then, sodium hydroxide was added to adjust pH close to 10, and blue color appeared again. The procedure was continue until the color of solution turn pale when adding sodium hydroxide to adjust pH. Finally, the product was almost copper hydroxide or metastable compound such as $Cu_4SO_4(OH)_6$. The filtrate contains trace quantity of copper and impurities as show in table 5.

According to Eh-pH diagram, the copper hydroxide system will form stable copper oxide at high pH value, the product of precipitation process was heated in alkaline solution. The pH of solution was adjusted to 12.0. Due to that a decrease will resulted in the formation of $Cu_4SO_4(OH)_6$. This can be proved by X-ray diffraction spectrum. In order to get pure copper oxide, pH of solution must be raised. Therefore, the reaction was operated again at pH = 12.75, and the pH was kept at 12.60 until reaction complete. The product was transformed copper oxide, and its crystal phase diagram was shown in fig. 3. The filtrate just contains 26.7 ppm aluminum that is favorable to purification of copper oxide. The purified product was analyzed and the result was shown in table 6. The recovery of copper from leachate is about 91.2% and the purity of copper oxide is 98.4%.

Stabilization of precipitation of metals hydroxide

The residue of leaehate precipitation experiment contains about 8.8% copper and other metals hydroxide. Because it may be harmful to the environment, the residue was treated by ferrite process in this research. The residue was placed in 500ml alkaline solution contained 0.25M Fe^{+2} in 1 liter vessel, aerated 5 hr at 80^0C. Then the black and magnetic ferrite was formed without other crystal phases in XRD diagram. The result was proved by X-ray diffraction spectrum shown in Fig. 4. in which these peaks shift a few degree toward high degree direction. It is appearance that impurity or metal ions were into spinel structure. And the composition of filtrate is listed in table 7. The impurity of residue can be almost eliminated by forming into spinel structure.

Conclusion

1. The recovery of copper by leaching of sludge is 85.4 at the operating conditions as follows: The ratio of dry solid content and sulfuric acid volume was controlled approximately at 1:10, placed it for 12 hr then stirred for 1 hr at 500 rpm, and the final leachate pH value was 3.20.
2. It is appearant that the concentration of copper increases with increasing pH. But other impurities will be precipitated as metal hydroxide. It reveals that the tendence to form ammine solution depend on pH since the speciation of ammonia in aqueous solution is determined by pH. When pH is adjust to 10, copper recovery is about 91.2% from leachate, and impurities except zinc are also severe decrease.
3. If the aeration reaction is not completed, $Cu_4SO_4(OH)_6$ may be formed in the solution.
4. The recovery of copper from leachate solution is about 91.2% and the purity of copper oxide is 98.4%.
5. The residue of metals hydroxide produced during precipitation can be treated by ferrite process to form stable oxide.

Acknowledgment

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References

[1]Industrial Development of Bureau Ministry Economic Affairs of R.O.C. 1996. Cases Symposium of Resource Recovery of PBC Manufacturing.

[2]Economic Affairs of R.O.C. 1997. Mineral Statistic Yearbook Taiwan Area.

[3]F. J. Alguacil. 1999. Recovery of Copper from Ammoniacal/Ammonium Carbonate Medium by LIX973N. Hydrometallurgy. 52:55-61

[4]Mehmet G, K.T. Hodgson, and E.L. Cussler. 1983. Selective Electrorefining with Liquid Membranes. AIChE. 29:144-149.

[5]Marcel Pourbaix. 1974. Atlas of Electrochemical Equilibria in Aqueous Solution.

[6] Oh Jaehyun. 1992. Removal of Heavy Metals from Waste Water by Ferrite Process.

[7]Jitka J., T. S., and R. N. 2000. Recovery of Cu-concentrates from Waste Galvanic Copper Sludges. Hydrometallurgy. 57:77-84

[8] Chin-Jung Chang, J.C. Liu. 1998. Feasibility of Copper Leaching from an Industrial Sludge using Ammonia Solutions. Journal of Hazardous Materials. 58:121-132.

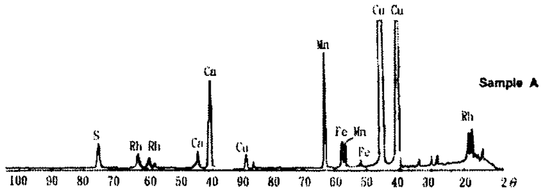

Fig. 1 XRF diagram of sample A

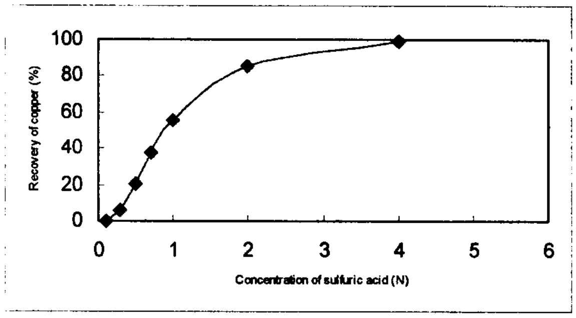

Fig. 2 Plot of copper recovery of sample A in sulfuric acid
(S/ L =1/10, and placed it 12 hr to stir 1 hr at 500 rpm.)

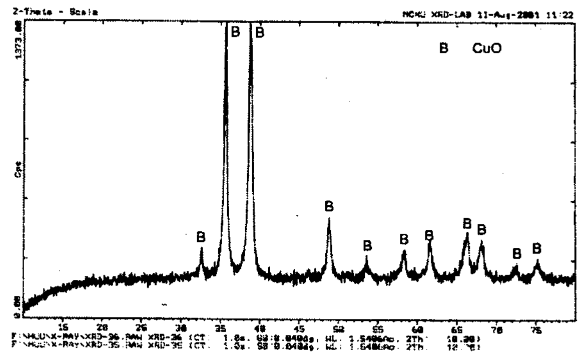

Fig. 3 XRD diagram of product produced by aeration reaction of sample A

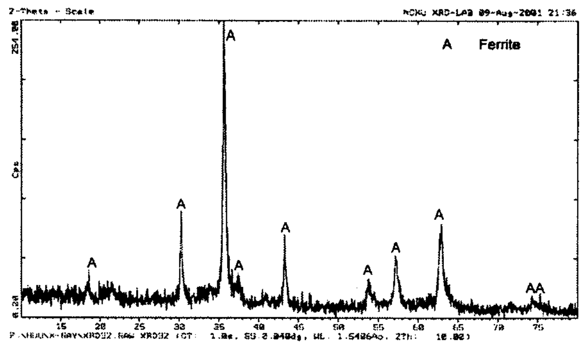

Fig.4 XRD diagram of stabilized residue

Table 1 Character of sludge

Sample no. / Character of sludge	A	B	C	D	E
Moisture (%)	82.7	63.7	76.0	88.2	60.0
pH of sludge	8.10	6.70	8.36	7.30	8.01
Cu (wt%)	18.40	18.90	17.50	22.6	45.8
Zn (wt%)	0.02	0.24	0.03	17.1	0.79
Pb (wt%)	0.11	--	--	N.D.	N.D.
Fe (wt%)	0.21	1.68	1.07	0.28	0.15
Ca (wt%)	0.31	1.00	0.65	0.46	0.63
Mn (wt%)	1.46	0.63	1.02	0.01	N.D.
Sn (wt%)	0.34	4.48	0.17	N.D.	0.06
Al (wt%)	8.1	--	--	1.7	0.07
Ni (wt%)	--	--	--	5.30	1.75
Cr (wt%)	--	--	--	2.90	0.34

-- no analysis
N.D. represents trace quantity

Table 2 TCLP results of sludge (ppm)

Element / Sample no.	Cu	Zn	Pb	Cr	Cd
A	37.4	0.1	1.6	N.D.	N.D.
B	242	1.9	N.D.	N.D.	N.D.
C	33.3	0.13	1.4	N.D.	N.D.
D	52.7	362.0	N.D.	N.D.	0.04
E	521.0	178.0	0.4	0.03	0.1
limitation	15	25	5	2.5	1

N.D. represents trace quantity

Table 3 Concentration of metal ions in sample A leachate (ppm)

Element / Sulfuric acid (N)	leachate pH	Cu	Pb	Zn	Fe	Mn	Sn	Ca
0.1	5.88	N.D.	N.D.	N.D.	N.D.	88.2	N.D.	132
0.3	4.49	602	2.4	1.0	N.D.	246.6	N.D.	143
0.5	4.15	2118	3.5	3.0	N.D.	347.2	N.D.	149
0.7	3.93	3895	4.5	4.0	0.3	434.4	N.D.	159
1.0	3.72	5755	5.1	3.9	1.6	528.0	N.D.	156
2.0	3.20	8895	6.3	4.5	37.4	534.4	4.96	148
4.0	0.31	10289	7.0	5.3	58.8	502.3	59.5	146

(S / L=1/10, and placed it 12 hr to stir 1 hr at 500 r)

Table 4 Composition of ammine at different pH (ppm)

element / pH	Cu	Pb	Zn	Fe	Mn	Sn	Ca	Al
7.10	536.1	1.9	0.1	N.D.	--	1.28	135	N.D.
7.58	1442.6	0.76	0.18	N.D.	--	N.D.	97.0	N.D.
8.07	2563.5	N.D.	0.26	N.D.	--	N.D.	87.7	1.9
8.48	5114.0	--	0.76	0.3	169.5	N.D.	--	7.9
9.01	6143.6	--	1.8	0.4	91.3	N.D.	--	22.0
9.55	6647.8	N.D.	2.9	0.1	60	N.D.	29.5	48.4
10.01	7653.4	0.5	5.5	1.0	59.7	1.0.	23.8	120

-- no analysis
N.D. represents trace quantity

Table5 Composition of filtrate produced in purification experiment of sample A

Element	Cu	Pb	Zn	Fe	Mn	Sn	Ca	Al
Concentration of Leachate(ppm)	8394.7	6.3	7	36.8	534.4	4.8	152	4780
Concentration of ammine(ppm)	7653.4	0.5	5.5	1.0	59.7	1.0	23.8	120
Concentration of filtrate removed ammonia (ppm)	1.7	0.38	0.5	N.D.	N.D.	N.D.	20.2	N.D.
Concentration of filtrate (1) (ppm)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	17.9
Concentration of filtrate (2) (ppm)	2.1	0.05	0.03	N.D.	0.05	N.D.	1.3	26.7

pH of ammine is10.0
N.D. represents trace quantity
(1) pH decrease from11.9 down to 10.8 during aeration
(2) pH decrease from12.75 down to 12.6 during aeration again

Table 6 Composition of CuO product (wt%)

Element sample	Cu	Pb	Zn	Fe	Mn	Sn	Ca	Al
Sample A	98.4	0.07	0.06	0.10	0.54	0.50	0.04	0.25

Table 7 Composition of filtrate after residue treated by ferrite process (ppm)

Element	Cu	Pb	Zn	Fe	Mn	Sn	Ca	Al
Concentration	N.D.	N.D.	0.6	N.D.	N.D.	N.D	10.8	29.7

$FeSO_4 \bullet 7H_2O$ 0.25M
pH of ammine is 9.53
N.D. represents trace quantity