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Feasibility of copper leaching from an industrial sludge using ammonia solutions

Chin-Jung Chang, J.C. Liu *

Department of Chemical Engineering, National Taiwan University of Science and Technology,
43 Keelung Road, Section 4, Taipei, 10672, Taiwan

Abstract

Feasibility study on the recovery of copper from an industrial sludge was conducted. The petrochemical sludge containing high concentration of copper was characterized utilizing X-ray diffractometer (XRD) and X-ray photoelectron spectroscopy (ESCA). Sequential extraction was used to determine the chemical forms of copper in the sludge. To leach copper from the sludge, aqueous ammonia solution was used. The leaching reaction was completed within 6 h. Best leaching efficiency (ca. 94%) was found at pH of 10. Higher solid–liquid ratio and higher temperature could enhance the leaching reaction. Results of the copper speciations in the leached sludge show that copper was mainly leached from both the organic-bound and residual fractions. Results suggested that the ammonia-leaching technique is full of potential in metal recovery from industrial sludges. © 1998 Elsevier Science B.V.

Keywords: Ammonia; Copper; Fractionation; Leaching; pH; Petrochemical; Sludge; Waste

1. Introduction

Accompanying the rapid industrial development in Taiwan, the petrochemical industry has become an important sector in the economy. The petrochemical industry also causes severe environmental pollution in Taiwan. It was estimated to contribute significant portions of wastewater (11%) and hazardous waste (32.8%) generated by manufacturers in Taiwan. Among a variety of hazardous waste generated, sludge is the one that troubles the petrochemical plants and calls for sound management. Although some factories have been implementing resource recovery and reuse, a majority still find it advantageous to precipitate the metals and discharge the waste water. Sludges containing

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* Corresponding author. Tel.: +886 2 737 6627; fax: +886 2 737 6644; e-mail: liu@ch.ntust.edu.tw

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heavy metals are collected in sedimentation tank, dewatered and then be solidified/stabilized before they are disposed. Considering that the sludge containing metals is often with potential economic value, there has been increasing concern on resource recovery of metals from the sludges. Nowadays, various technologies are available to manufacturers to handle these sludges: recovery of copper by crystallization [1], electrochemical recovery of copper [2] and recovery of copper by an ammonia leach or an acid leach [3–6]. The incentives for metal recovery include [3]:

(i) creation of metal credits to offset treatment cost,
(ii) waste minimization and resource conservation,
(iii) avoiding liability for generating hazardous waste.

The major objective of the current study is to investigate the feasibility of leaching Cu from a petrochemical sludge using ammonia solutions. It has been indicated that ammonia's low cost, availability and selectivity make it attractive. Meanwhile some research has focused on leaching of copper from soil using anhydrous ammonia [7]. Many parameters, such as pH, redox potential, solid–liquid ratio, temperature and chelates, will affect the leaching behaviors of heavy metals from sludges. Among them, both pH and chelates have long been recognized as critical parameters controlling the reactions. Theoretical prediction of heavy metal equilibria as affected by pH and chelates has been extensively studied. It is critical to the assessment of feasibility of leaching metals as a potential measure to recover valuable resources and is believed to be beneficial in detoxifying sludges.

2. Materials and methods

2.1. Characterization of the sludge

Sludge sample was obtained in June of 1995 from the wastewater treatment plant of a chemical plant within the petrochemical industrial park in Kao-Hsiung County, Taiwan. Dewatered sludge was sampled from the filter press. The sample was oven-dried at 50°C for 24 h. It was ground with a mortar and then sieved. The fraction between 40–50 mesh was retained and stored in a PE bottle for the study. Size distribution of the sludge (Fig. 1) was determined utilizing a sizer (Malvern 2600 C). The scanning electron microscope analysis (Cambridge S360) showed the sludge consisted of aggregated small particles with irregular shape (Fig. 2A). Semi-quantitative surface content by energy-dispersive analysis showed (Fig. 2B) that Ca, Al, Fe, Ti, V, Zn and Cu are major components. The crystal structures of the sludge sample (Fig. 3) was analyzed by an X-ray diffractometer (Philips MP-710). The sludge sample was first vacuum dried at 120°C and then scanned from 10 to 70° at the voltage of 40 kV. The results showed the sludge was amorphous and no crystal form could be identified. The surface composition of the sludge was analyzed by a photoelectron spectroscope (ESCA). The sludge sample was vacuum dried at 120°C, pressed (Jasco, TP-100) into a pellet with a diameter of 10 cm and then glued to the acetone-washed holder. When analyzed by the ESCA (VG Microtech, MT-500), the pressure was kept at 2×10^{-8} Torr, anode volts at 15 kV and the emission current at 20 mA. The results showed that there are peaks of Ca, Cu, Fe, Al and Cr (Fig. 4). The

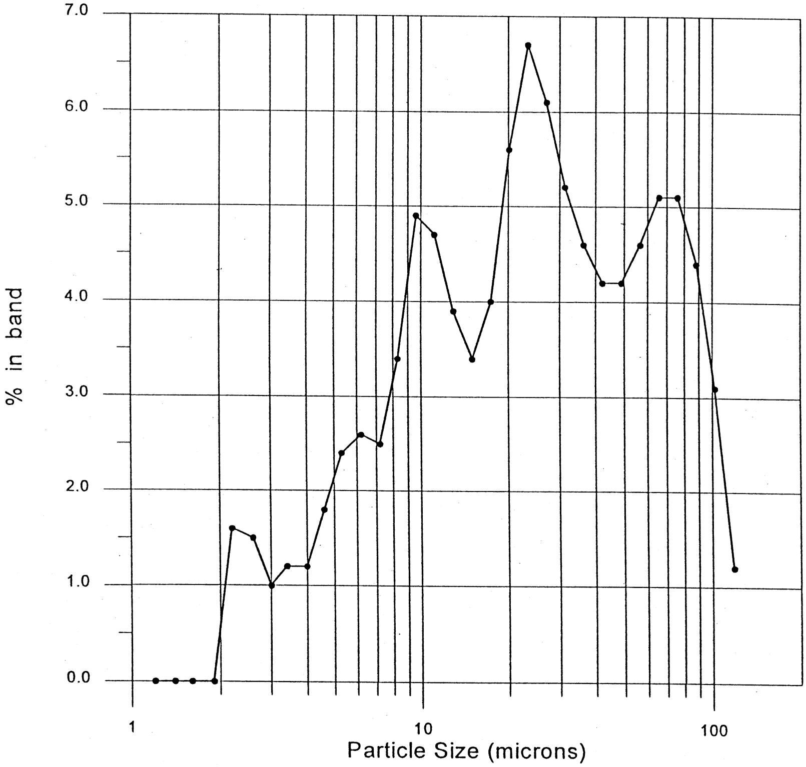


Fig. 1. Size distribution of the sludge.

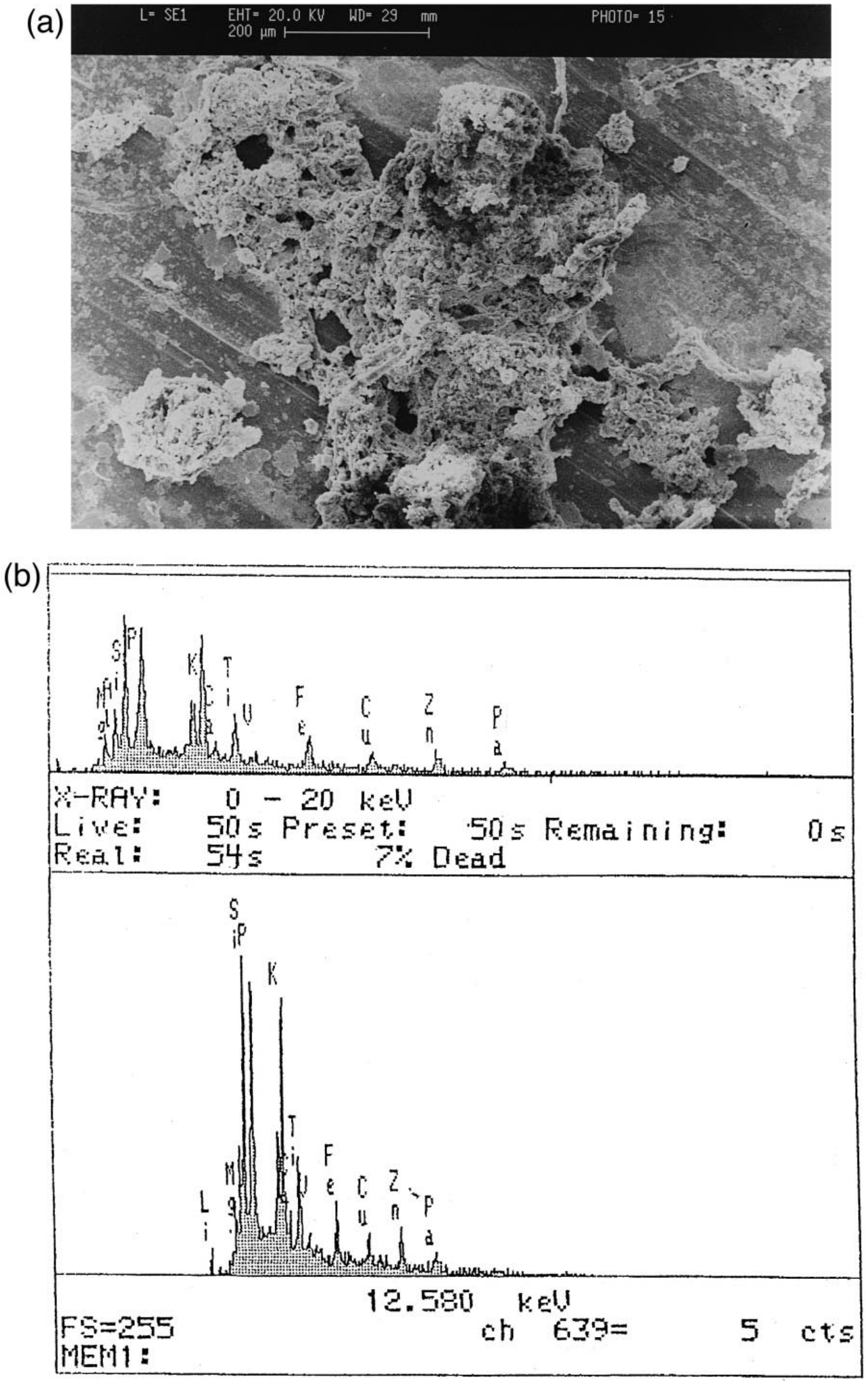
electrical property of the sludge surface was characterized with a zeta meter (Photal, LEZA-600). The zero-point-of-charge (ZPC) was found at 2.6 (Fig. 5).

In order to analyze total metal content [8], 5.0 g of sludge was placed in a 250 cm^3 pyrex flask filled with 50 cm^3 of distilled water. A total of 5 cm^3 of 4 N HNO_3 (Naclai Tesque) was added to the sludge suspension and then placed on a heating plate (Corning PC-320) for digestion. A small amount of nitric acid was added intermittently to prevent sludge from total dry-out; until the supernatant became clear and a brownish-colored fume no longer generated. The suspension was cooled and filtered through a 0.45 μm membrane filter (MFS) and then measured by an atomic absorption spectroscopy (GBC 904). The results are summarized in Table 1.

In the metal fractionation experiment, sequential extraction procedures [9] were utilized. The scheme is displayed in Table 2. Copper was partitioned into exchangeable, carbonates-bound, Fe–Mn oxides-bound, organic-bound and residual fractions.

2.2. Experimental set-up and procedure

To study the leaching behavior of Cu from the sludge using ammonia solution, a reactor (Pyrex 4280) equipped with a stirrer (Fargo) was used (Fig. 6). Appropriate



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X-RAY:     0 - 20 keV
Live:     50s Preset:    50s Remaining:     0s
Real:     54s        7% Dead
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                    12.580  keV
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Fig. 2. (a) Scanning electron microscope picture of the sludge. (b) Energy-dispersive spectrometric analysis of surface content of the sludge.

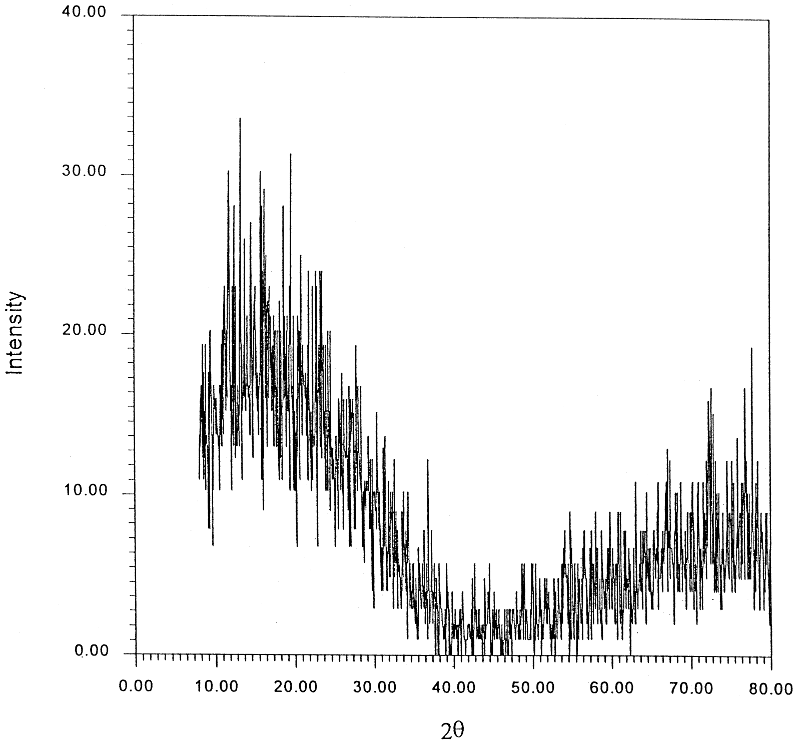


Fig. 3. X-Ray diffraction (XRD) spectrum of the sludge.

amount of distilled water was placed into the reactor, measured volume of ammonia solution (28–30 wt.%, Acros) was added. The pH of suspension was adjusted with concentrated HNO_3 and then controlled at preset value of 10.0 by a potentiostat (KEM APB-410). Sludge was then added. Each time 10 cm^3 of sludge suspension was sampled at certain time interval. After the sample was filtered through 0.45 μm membrane filters (MFS), the Cu concentrations were determined by an atomic absorption spectroscopy.

Next, effects of leaching on the speciation of Cu in the sludge were assessed. The leached sludge was filtered and rinsed with distilled water several times. It was dried at 105°C in an oven for 24 h. One gram of sludge was used for sequential extraction.

3. Results and discussion

3.1. Leaching experiment

Based on the characteristics of the sludge, Cu was selected as the target metal for recovery. The leaching kinetics of Cu from the sludge was conducted with pH value of 10.0. The concentration ratio of NH_3(aq) and Cu(aq) was equal to 5 (molar basis) and the solid concentration was 10 g/l. The leaching reaction was isothermal at 20°C. The

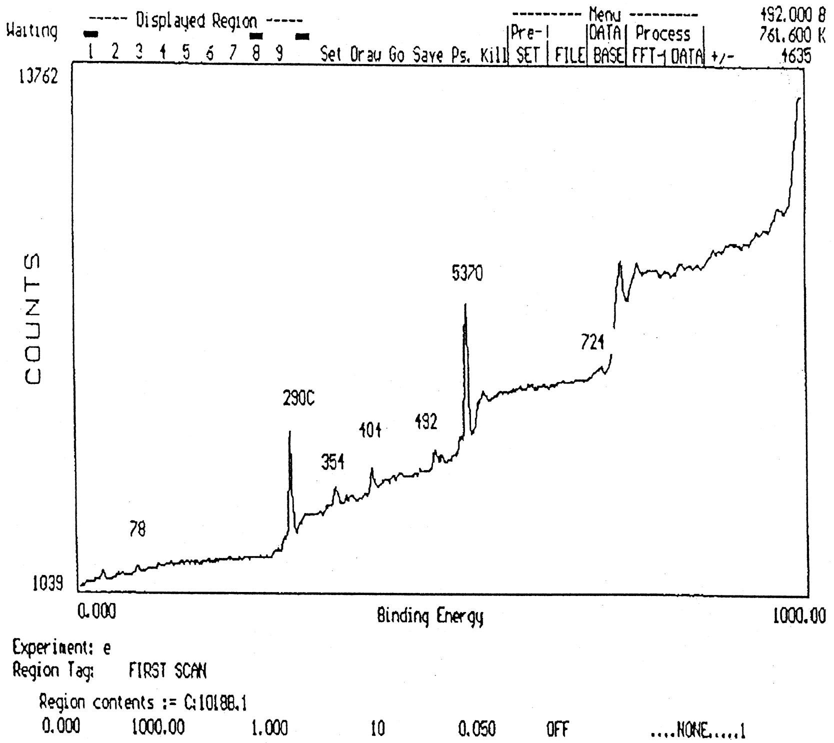


Fig. 4. X-Ray photoelectron (ESCA) spectrum of the sludge.

total concentration of Cu was derived from the digestion experiment. The results are shown in Fig. 7. It was found that the leaching reaction was very fast in the first stage and stabilized afterwards. Most of the reactions were completed within 6 h. Total of 34% of Cu was leached out. The leaching efficiency was significantly increased to ca. 94% when the reaction was at 25°C and the solid concentration was increased to 20 g/l (Fig. 8). The mechanism of the leaching reaction is in principle the complexation reaction between Cu(II) and ammonia solution. This leaching efficiency is dependent on pH since the speciation of ammonia in aqueous solution is determined by pH. Acknowledged that the acidity constant (K_a) of NH_4^+(aq) equals to $10^{-9.3}$, the major species is NH_4^+(aq) when pH is lower than 9.3. The complexation reaction of Cu^{2+}(aq) can occur only with NH_3(aq), not with NH_4^+(aq). The reaction is as follows [10]:

$$Cu^{2+} + NH_3 \leftrightarrow Cu(NH_3)^{2+};\ pk = 4.0$$

$$Cu^{2+} + 2NH_3 \leftrightarrow Cu(NH_3)_2^{2+};\ pk = 7.5$$

$$Cu^{2+} + 3NH_3 \leftrightarrow Cu(NH_3)_3^{2+};\ pk = 10.3$$

$$Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{2+};\ pk = 11.8$$

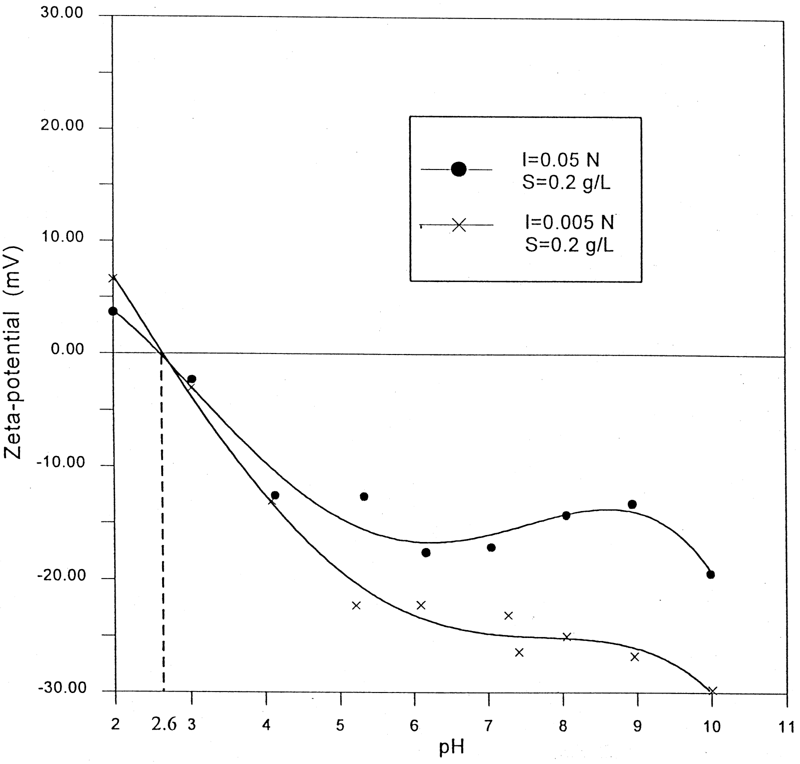


Fig. 5. Zeta potential of the sludge as a function of pH: ionic strength $(I) = 0.005$ N $NaNO_3$ and 0.05 N $NaNO_3$, solid concentration $(S) = 0.2$ g/l, 25°C.

The pure Cu can further be separated from the Cu–ammonia complexes. The conceptual design for the following process units include filtration, pH adjustment, vaporization and recycle of ammonia. The toxicity of sludge is expected to be greatly decreased as a result of the high-efficiency leaching of Cu. Thus, the advantages of the present study are in principle the recovery of Cu and the detoxification of the hazardous sludge.

3.2. Fractionation experiment

Most studies dealing with sludge containing heavy metals discuss total metal concentration without attempt to evaluate various chemical forms in which metals exist.

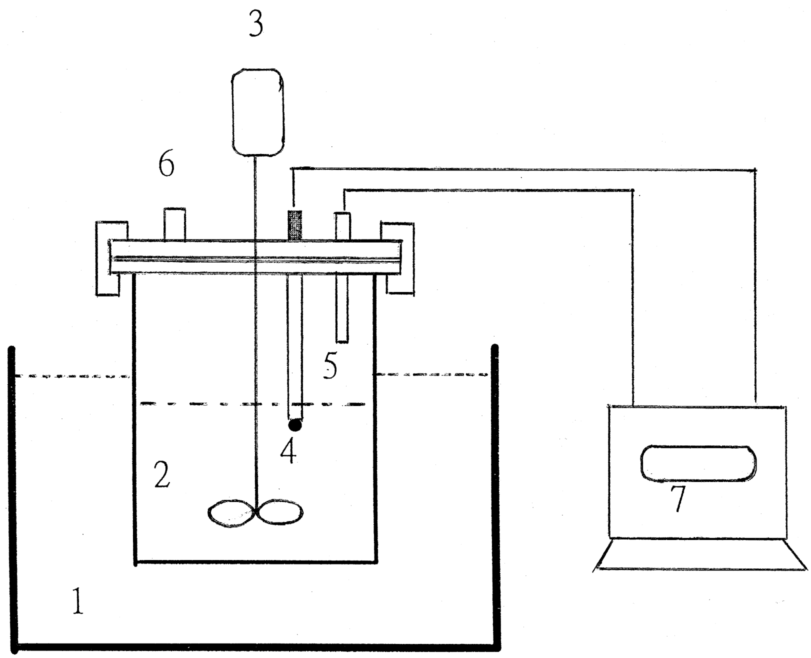
Table 1
Metal contents of the sludge (mg/kg)

Cu	Fe	Zn	Pb	Cr	Ni
42630	7383	1502	308	266	68

Table 2
Sequential extraction procedures

Fraction	Extractant	Extraction condition
Exchangeable	10 ml 1 M $MgCl_2$	Shaken 1 h at pH = 7
Carbonates-bound	10 ml 1 M NaOAc	Shaken 5 h at pH = 5
Fe–Mn oxides-bound	20 ml 0.04 M $NH_2OH \cdot HCl$	Shaken 5 h at 85°C
Organic-bound	20 ml 30% H_2O_2 and 10 ml conc. H_2SO_4	Shaken 2 and 3 h, respectively, at 85°C
Residual	20 ml conc. H_2SO_4	Mildly boiled for 1 h

The chemical forms of Cu in the solid phase can greatly influence its fate in terms of leaching and subsequent transport [11]. The sequential extraction procedure has been utilized to evaluate chemical forms of heavy metals in sludge-amended soil [12–14] and sludges [11,15]. In order to investigate the leaching mechanism and the changes of Cu speciation after the leaching experiment, sludge which had been leached under pH of



1. Isothermal water bath
2. Leaching tank
3. Stirrer
4. pH probe
5. Acid or base input
6. Sampling port
7. Potentiostat

Fig. 6. Experimental apparatus for the leaching study.

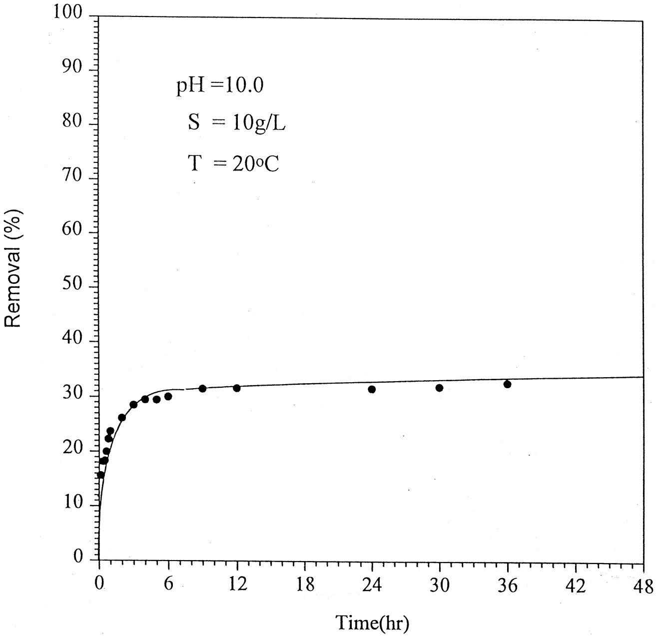


Fig. 7. Cu leaching: pH = 10.0, *S* = 10 g/l, 20°C.

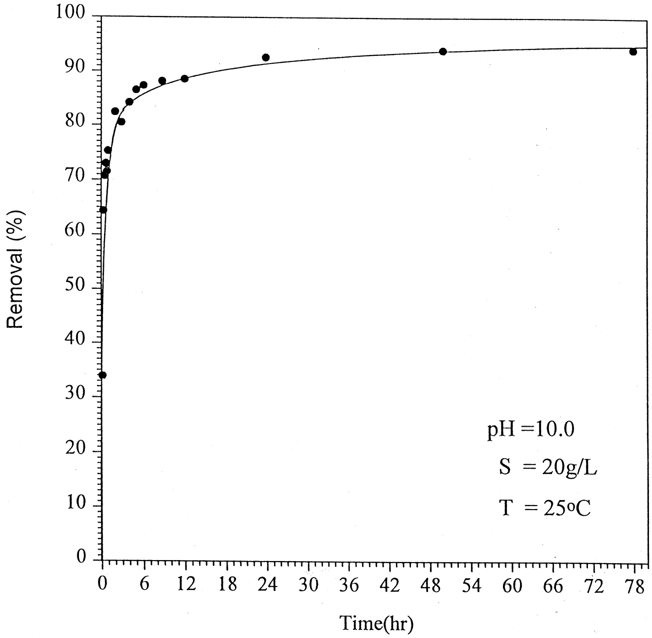


Fig. 8. Cu leaching: pH = 10.0, *S* = 20 g/l, 25°C.

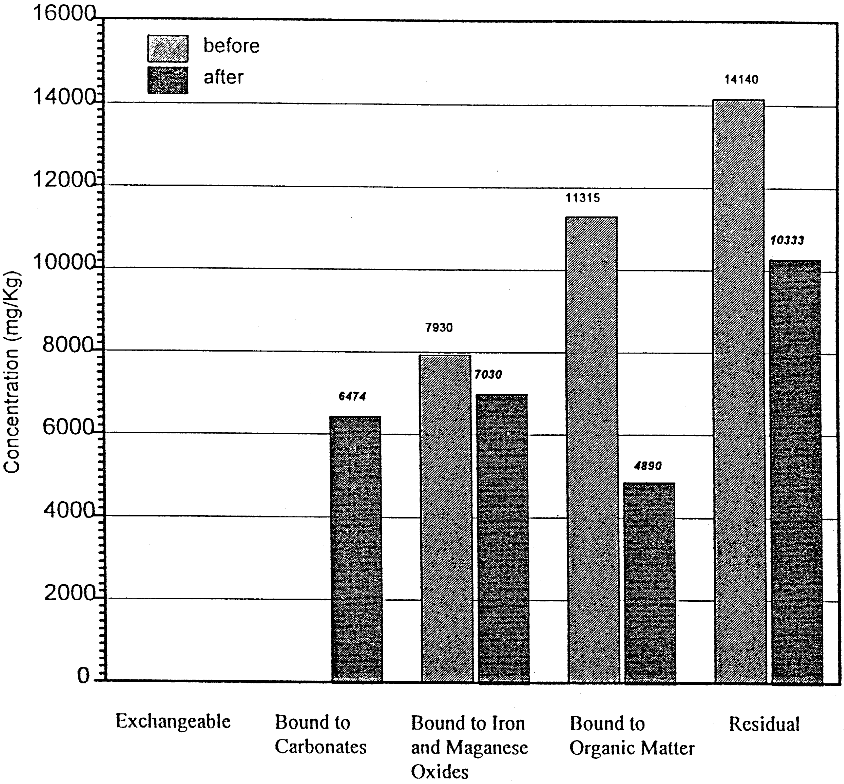


Fig. 9. Cu fractionation in the sludge before and after the leaching experiment.

10.0 and solid concentration of 10 g/l at 20°C was examined on the fractionation of Cu. Results are shown in Fig. 9. In the unleached sludge, the residual fraction of Cu was the most dominant (42.3%); while both Fe–Mn oxides-bound Cu (33.8%) and carbonates-bound (23.7%) constituted the other fractions. The fractionation changed significantly after the leaching reaction. The residual fraction was still the most abundant one (36.0%). Whereas, the organic-bound Cu decreased to 17% and the Fe–Mn oxides-bound Cu decreased to 24.5%, respectively. It is notable that the carbonates-bound fractions of Cu increased during the leaching procedure. The sequential extraction procedure provides qualitative information that may allow for the prediction of the biological availability, mobilization and transport. However, little work has been conducted on the effect of ligand and the subsequent complexation reaction on changes of fraction and the mobility of heavy metals. In studying lake sediment, oxidation has been found to cause changes of fraction and related mobility of heavy metals [16]. Similar findings have also been shown among tannery waste and sludge-amended soils [14]. The changes in the chemical forms of Cu in the petrochemical sludge before and after the leaching experiment are affected by the presence of ammonia and the change in pH value. However, judging from the significant decrease of portions of the two least mobile fractions, i.e. organic-bound and residual fractions, it is proposed that the leaching of Cu could well be related to changes of fractionation. Nevertheless, further study is definitely required to delineate the correlation.

4. Conclusion

As land disposal of petrochemical wastes continue to represent an attractive option in Taiwan, questions regarding resource recovery may be raised. Little information has been published on leaching behaviors of metals from petrochemical sludge. Based on results obtained from the current work, the following conclusions are made:

The sludge can be characterized as a heterogeneous mixture containing metal precipitates in amorphous form. The ZPC of the sludge is 2.6. The high Cu content rendered the sludge hazardous.

Results from sequential extraction showed that residual, organic-bound and Fe–Mn oxides-bound fractions constituted the majority of Cu. Fractionation pattern is expected to affect leaching of Cu.

Total of 35% of Cu was leached out with ammonia solution. The leaching efficiency could be increased to 94% by increasing the solid concentration and temperature.

The fractionation of Cu in the leached sludge changed significantly. The carbonates-bound fraction of Cu increased, while Cu in the other fractions decreased.

Acknowledgements

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References

[1] M. Scholler, J.C. van Dijk, D. Wilms, Recovery of heavy metals by crystallization, Metal Finishing, Nov., 1987, pp. 31–34.

[2] H.E. Allen, P.H. Chen, Remediation of metal contaminated soil by EDTA incorporating electrochemical recovery of metal and EDTA, Environ. Prog. 12 (1993) 284–293.

[3] R. Jadvar, B.J. McCoy, B. Ford, J. Galt, Recovery of gallium and arsenic from GaAs wafer manufacturing slurries, Environ. Prog. 10 (1991) 278–281.

[4] C.S. Brooks, Recovery of nonferrous metals from metal finishing industrial wastes, Sep. Sci. Technol. 28 (1993) 579–593.

[5] C.H. Lu, R. Wang, W.J. Yang, D.C. Liu, Extracting Cu, Ni and Zn from sludge with ammonium carbonate, Proc. 9th Conf. on Waste Management Technology in ROC, Taichung, Taiwan, Nov., 1994.

[6] A. Rivoallan, M. Calmettes, M. Cohendet, Recovery and recycling of heavy metals in industrial sludges, Resour. Conserv. Recycl. 10 (1994) 177–184.

[7] D.A. Clifford, M. Yang, T. Nedwed, Feasibility of extracting toxic metals from soil using anhydrous ammonia, Waste Manage. 13 (1993) 207–219.

[8] Standard Methods for the Examination of Water and Wastewater, 16th edn., APHA, AWWA, WPCF, Washington, DC, 1985.
[9] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedures for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–851.
[10] M.M.F. Morel, J.G. Hering, Principles and Applications of Aquatic Chemistry, Wiley, New York, 1993.
[11] T.E. Clevenger, Use of sequential extraction to evaluate the heavy metals in mining wastes. Water Air Soil Pollut. Vol. 50, 1990, pp. 91–96, 241–254.
[12] J.T. Sims, J.S. Kline, Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge, J. Environ. Qual. 20 (1991) 387–395.
[13] S. Dudka, A. Chlopecka, Effect of solid-phase speciation on metal mobility and phytoavailability in sludge-amended soil, Water Air Soil Pollut. 51 (1990) 153–160.
[14] R. Milacic, J. Stupar, Fractionation and oxidation of chromium in tannery waste and sewage sludge-amended soils, Environ. Sci. Technol. 29 (1995) 506–514.
[15] H.A. Elliot, B.A. Dempsey, P.J. Maille, Content and fractionation of heavy metals in water treatment sludges, J. Environ. Qual. 19 (1990) 330–334.
[16] K. Saeki, M. Okazaki, S. Matsumoto, The chemical phase changes in heavy metals with drying and oxidation of the lake sediments, Water Res. 27 (1993) 1243–1251.