



Effect of $[\text{Fe}^{2+}/\text{total metal}]$ on treatment of heavy metals from laboratory wasteliquid by ferrite process

Yuh-Jeen Huang^{a,*}, Chiu-Hui Tu^b, Yi-Chi Chien^c, Hung-Ta Chen^d

^aDepartment of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, Hsinchu, Taiwan 300, ROC

^bDepartment of Occupational Safety and Health, Chung Hwa College of Medical Technology, Tainan Hsien, Taiwan 717, ROC

^cDepartment of Environmental Engineering, Fooyin University, Kaohsiung Hsien, Taiwan 831, ROC

^dEnvironmental Resource Management Research Center, National Cheng Kung University, 1, University Rd., Tainan, Taiwan 701, ROC

Accepted 9 November 2005

Abstract

In this study, the X-ray absorption near-edge structure shows that poisonous Cr^{6+} in the laboratory wasteliquid were reduced to Cr^{3+} by adding Fe^{2+} at $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio higher than 4:1. The X-ray diffraction analysis shows that greater the $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios used (such as 6:1, 10:1, 20:1 and 30:1), the more spinel-structured ferrites were formed (0.26, 0.30, 0.48 and 0.59). When $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio was larger than 20:1, the saturation magnetization and coercive field were about 5.21 emu/g and 6.2 kOe, respectively. The ferrite precipitates could be recovered as magnetic materials. However, the TCLP test result was beyond the standard of EPA when the $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio was 30:1. The optimum operation for the laboratory wasteliquid by ferrite process in the $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio was 20:1.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Ferrite; Heavy metals; XRD; XANES; Laboratory wasteliquid

1. Introduction

Laboratory wasteliquid is of multiple varieties, is available in small quantities, ambiguously classified, which makes it very difficult for contractors to dispose them of. Most laboratories use storage tanks to store the wasteliquid residues left from experiments. Within a few years, it will become a serious problem on campuses, and many schools have no choice but to encounter.

Many studies have been made on removing heavy metals in solution (McNeill and Edwards, 1997; Mandaokar et al., 1994; Benjamin et al., 1982). In the

ferrite process, Fe^{2+} would be partially oxidized by air to produce Fe_3O_4 in alkaline solution (Barrado et al., 1998). The heavy metals such as Ni, Mn, Mg, Zn, Cr and Pb could be involved into the lattices of the ferrites to form the spinel-structured ferrites by the oxidation of Fe^{2+} . Thus, the ability of recovering heavy metals and forming magnetic precipitates make the ferrite process suitable for treating laboratory wasteliquid.

X-ray absorption spectrum (XAS) is very useful in the identification of the environment, degree of aggregation or location of metal elements (Yamashita, et al., 1996; Stern et al. 1995; Gaskell et al., 1982). X-ray absorption near-edge structure (XANES) holds out the possibility of obtaining new information, both electronic and structural. In this study, XANES could be used to observe the change of valence between Cr^{6+} and Cr^{3+}

*Corresponding author. Tel.: +886 3 5715131x35496;
fax: +886 3 5718649.

E-mail address: yjhuang@mx.nthu.edu.tw (Y.-J. Huang).

as well as the behavior of ferrite formation in the process. Spinel structure and magnetic properties of ferrite were also studied by X-ray diffraction (XRD) spectroscopy and vibrating sample magnetometer (VSM). The stabilization efficiency of the ferrite process was evaluated from the TCLP test.

2. Experimental

2.1. Materials

The laboratory wasteliquid containing various heavy metals were obtained from a university in Tainan. The chemicals ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH) were analytically graded.

2.2. Apparatus

Many instruments were used in this experiment, e.g., pH meter (Metler Toledo, InLab 415), oxidation–reduction potentials (ORP) meter (Metler Toledo), oven (Mettmert), heater (Thermalyne, Cimarec3), vacuum filtration apparatus, thermal-control meter (Fargo Instruments, CA-400) and XRD (Siemens, D5000).

A vibrating sample magnetometer (VSM, DMS 1660) operating at room temperature with applied magnetic fields up to 16,000 Oe was used to measure the magnetic properties of each type of the metal particles.

XANES spectra of the samples and model compounds such as $\text{K}_2\text{Cr}_2\text{O}_7$ (Aldrich, Chemical Company), Cr_2O_3 (99%, Aldrich, Chemical Company), Cr foil and FeCr_2O_4 (ferrite) were recorded on the Wiggler beamline of the Taiwan National Synchrotron Radiation Research Center (NSRRC). The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter.

The toxicity characteristic leaching procedure (TCLP) test was carried out according to the EPA method of Taiwan. A 5.00 ± 0.01 g dried precipitates generated from ferrite process was extracted with appropriate buffered acetic acid for 18 ± 2 h. The concentrations of chromium, lead, copper and silver were analyzed by atomic absorption spectrophotometer (AAS).

2.3. Procedure

The heavy-metal wasteliquid of laboratory was mixed with different $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio between 6:1, 10:1, 20:1 and 30:1 in the beaker. When mixed thoroughly, the wasteliquid was adjusted to $\text{pH} = 9$. The condition of wasteliquid was detected by X-ray absorption spectroscopic measurements. The contents of the beaker was heated by water bath at 343 K. At the same time, the wasteliquid was aerated (the aeration rate

was 4 L/min) and its oxidation–reduction potentials detected using ORP meter. Finally, the precipitate formed was separated from the liquid phase by vacuum filtration apparatus and was put into the oven at 343 K for 8 h. The filtrates and the precipitates were subjected to AAS analysis. The precipitates were analyzed by XRD spectroscopy, VSM and TCLP test.

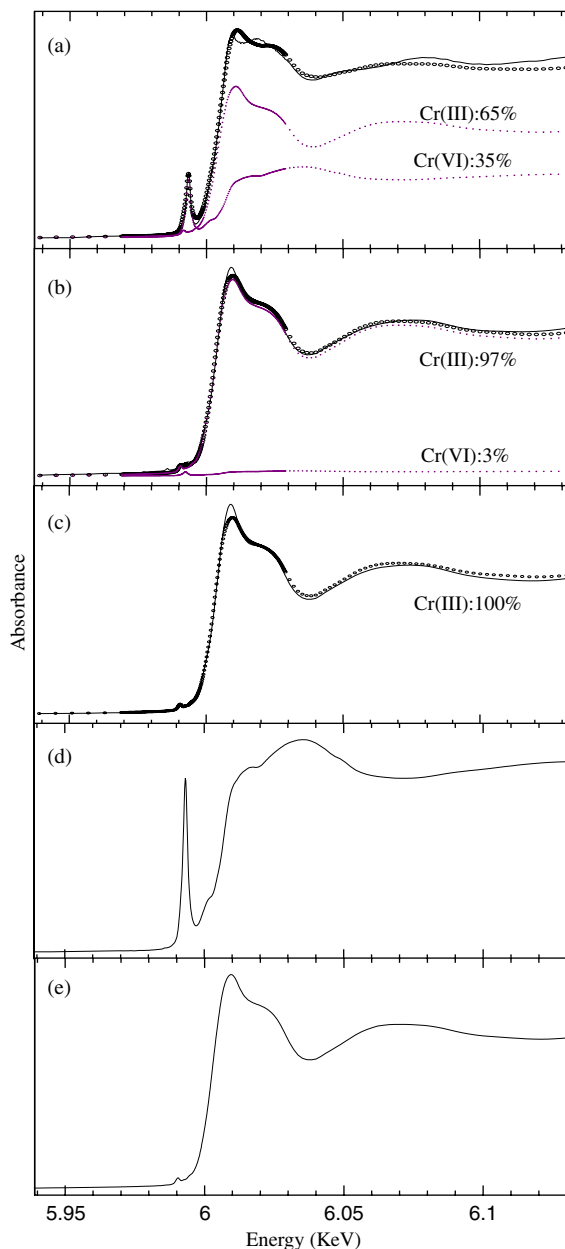


Fig. 1. Chromium XANES spectra of (a) original laboratory wasteliquid, and laboratory wasteliquid by ferrite process at the $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios of (b) 1:1, (c) 4:1, (d) the standard spectrum of $\text{K}_2\text{Cr}_2\text{O}_7$ and (e) the standard spectrum of Cr_2O_3 .

3. Results

XANES (Fig. 1(a)) shows that the percentages of Cr^{6+} and Cr^{3+} in the original laboratory wasteliquid were 35% and 65%, respectively. The poisonous Cr^{6+} was not reduced to Cr^{3+} completely at $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio of 1:1 (shown in Fig. 1(b)). It can be found that there still were 3% of poisonous Cr^{6+} and 97% of Cr^{3+} in the precipitates. All of the poisonous Cr^{6+} were reduced to Cr^{3+} by adding Fe^{2+} at $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio higher than 4 (see Fig. 1(c)).

Cr^{6+} could be reduced to Cr^{3+} directly by adding Fe^{2+} during the experiment. They could join together to form Cr ferrites, which could be observed as Cr_2FeO_4 in the X-ray diffraction pattern. Fig. 2(e) shows the characteristic spectrum of Cr_2FeO_4 . By using standard spectrum to fit in, it can be found that there was a great influence on different mole ratios of FeSO_4 . It can be found in the XRD that the production rate of ferrite at different $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios such as 6:1, 10:1, 20:1 and 30:1 were 0.26, 0.30, 0.48 and 0.59, respectively. Greater the $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios

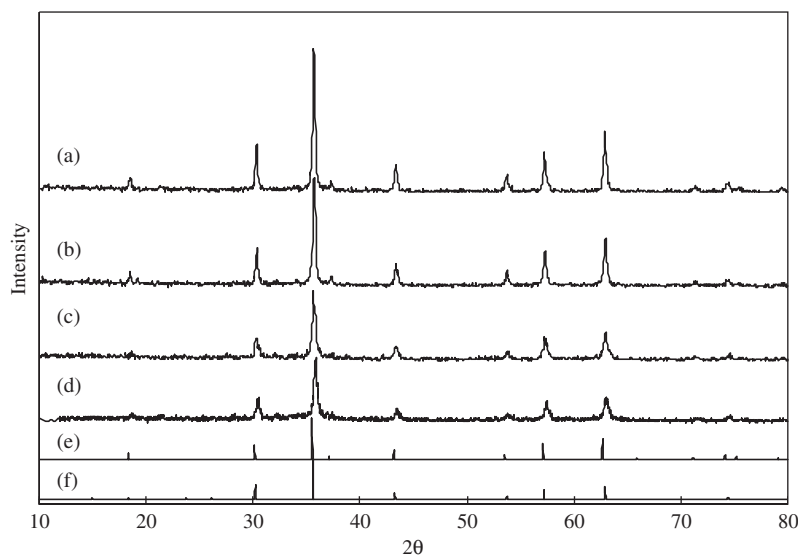


Fig. 2. X-ray diffraction pattern of chromium ferrite collected by laboratory wasteliquid at various $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios of (a) 30:1, (b) 20:1, (c) 10:1, (d) 6:1, (e) the standard spectrum of Cr_2FeO_4 and (f) standard spectrum of Fe_2O_3 .

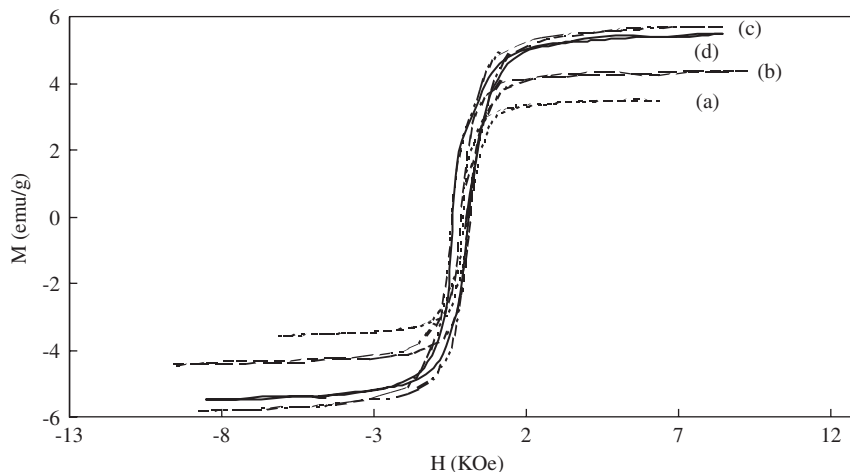


Fig. 3. The hysteresis loops measured from precipitates generated from ferrite at $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios (a) 6:1, (b) 10:1, (c) 20:1 and (d) 30:1.

Table 1

Toxicity characteristic leaching procedure (TCLP) test results for the precipitates generated from laboratory wasteliquid by ferrite process at various $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios

Heavy metals	Initial concentration of heavy metals in the laboratory wasteliquid (ppb)	TCLP test results for the precipitates generated by ferrite process at various $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios(ppb)				TCLP standards of EPA (ppm)
		6:1	10:1	20:1	30:1	
Total chromium	343000.0	6671.0	104.0	862.0	13800.0	5.0
Lead	20.9	6.9	10.4	36.8	4.8	5.0
Copper	98.5	71.8	55.4	45.2	59.6	15.0
Silver	90.5	9.1	12.5	3.8	2.7	5.0

were used, the more spinel-structured ferrites were formed.

The hysteresis loops measured from precipitates generated from ferrite at different $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios a shown in Fig. 3. When $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio lower than 6 contains 26% of ferrite, it had a lower magnetization of about 3.49 emu/g and a smaller coercive field of about 3.6 KOe (is shown in Fig. 3(a)). The saturation magnetic moment per gram and the width of the hysteresis loops were increased with the ratios of ferrite in the precipitates. When $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio was larger than 20:1 (contains more than 48% of ferrite), the saturation magnetization and coercive field were about 5.21 emu/g and 6.2 kOe, respectively.

Although the saturation magnetization of the precipitates is good to be recovered as magnetic materials, the stabilization efficiency of the ferrite process must be evaluated from the TCLP test. The concentrations of heavy metals in the TCLP extracts was shown in Table 1. Most of them were in accordance with the TCLP standard of EPA. It was worth to note that the TCLP test result was beyond the standard of EPA when the $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio was 30:1. The precipitates would be considered as hazardous waste. Thus, the optimum operation for the laboratory wasteliquid by ferrite process in the $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio was at 20:1.

4. Conclusions

The ferrite process can effectively remove heavy metals from laboratory wasteliquid. Poisonous Cr^{6+} could be reduced to Cr^{3+} by adding Fe^{2+} at $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio higher than 4:1. The XRD shows that the production rate of ferrite at different $[\text{Fe}^{2+}/\text{total metal}]$ mole ratios such as 6:1, 10:1, 20:1 and 30:1 were 0.26, 0.30, 0.48 and 0.59, respectively. When $[\text{Fe}^{2+}/\text{total metal}]$ mole ratio was 20:1, the saturation magnetization and coercive field were more than 5.21 emu/g and 6.2 kOe, respectively. The wastes will be regenerated as

Cr ferrites and can be reused. In this study it is suggested the ferrite process be applied to treat heavy metals from laboratory wasteliquid and solve the serious problems on campus.

Acknowledgments

The financial support of the National Science Council (93-2211-E-273-001), Taiwan, is gratefully acknowledged. We also thank Dr. Jyh-Fu Lee of the National Synchrotron Radiation Research Center for his XANES experimental assistance.

References

- Barrado, E., Prieto, F., Vega, M., Fernandez-Polanco, F., 1998. Optimization of the operational variables of a medium scale reactor for metal containing wastewater. *Water Res.* 32 (10), 3055–3061.
- Benjamin, M.M., Hayes, K.F., Leckie, J.O., 1982. Removal of toxic metals from power generation waste streams by adsorption and coprecipitation. *J. Water Pollut. Control Fed.* 54, 1472–1481.
- Gaskell, P.H., Glover, D.M., Livesey, A.K., Durham, P.J., Greaves, G.N., 1982. Near-edge and EXAFS studies of amorphous palladium–germanium. *J. Phys. C* 15 (19), L597–L604.
- Mandaokar, S.S., Dharmadhikari, D.M., Dara, S.S., 1994. Retrieval of heavy metal ions from solution via ferritisation. *Environ. Pollut.* 83 (3), 277–282.
- McNeill, L.S., Edwards, M., 1997. Arsenic removal during precipitative softening. *J. Environ. Eng.-ASCE.* 123 (5), 453–460.
- Stern, E.A., Newville, M., Ravel, B., Yacoby, Y., Haskel, D., 1995. The uwxafs analysis package—philosophy and details. *Physica B* 209, 117–120.
- Yamashita, H., Matsuoka, M., Tsuji, K., Shioya, Y., Anpo, M., Che, M., 1996. In situ XAFS, photoluminescence, and IR investigations of copper ions included within various kinds of zeolites—structure of Cu(I) ions and their interaction with Co molecules. *J. Phy. Chem.* 100, 397–402.