

Stabilization of heavy metals in municipal solid waste incineration ash using mixed ferrous/ferric sulfate solution

Shao-Hua Hu

Department of Resource Engineering, Dahan Institute of Technology,
Hualien 971, Taiwan

Received 19 November 2004; received in revised form 20 February 2005; accepted 21 March 2005
Available online 23 May 2005

Abstract

The purpose of this study is to test the effectiveness of mixing FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ solutions with municipal solid waste incineration (MSWI) ash at room temperature to prevent heavy metals in treated ash from being dissolved. After conducting toxicity characteristic leaching procedure (TCLP) tests nine times, the accumulation of extracted lead from treated scrubber ash was lower than regulated limits by the sixth test. X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive spectrometer (SEM/EDS) studies of the ash revealed that the mixed solution reacted with the scrubber ash to form $\text{Ca}_4\text{Fe}_9\text{O}_{17}$, which coated the surface of ash particles.

© 2005 Elsevier B.V. All rights reserved.

Keywords: MSWI; Heavy metal; Scrubber ash; Stabilization; TCLP

1. Introduction

According to Environmental Protection Agency (EPA) data in Taiwan, the amount of collected and transferred municipal solid waste (MSW) in 1982 was estimated to be about 3.8 million tons. The EPA also predicted that the quantity of MSW would exceed 10 million tons by 2001 if the growth rate of waste remained at 5% per annum [1]. A successful resource recycle policy was promoted in the ensuing years, so that the quantity of MSW decreased by millions of tons. However, although the policy was effective in reducing MSW about 6.7 million tons of such waste still required proper treatment. Over the period 1990–2003, the EPA initiated a program to deal with MSW by setting up 21 incinerator systems.

Incineration systems have been broadly adopted by local authorities as an important waste management technology. However, currently MSWI residues are running at about 22% of MSW [2]. The amount of residues containing bottom ash (i.e., that quenched from the bottom of the furnace), fly ash

(i.e., that collected by air cyclone), and scrubber ash (i.e., lime based scrubber ash) is about 1.8 million tons annually. The ratio of the above residues is 20:1:5 [3]. Both the bottom and fly ash are recovered by physical and chemical methods, such as magnetic separation, eddy current separation, water soaking, and ferrite coating, all of which has been discussed in previous studies [3]. However, scrubber ash, which is collected from flue gas, continues to pose serious environmental problems according to existing air pollution evaluation and control devices. Scrubber ash is usually classified as toxic waste owing to its frequent heavy metal content (Pb, Zn and Cd) that can exceed legal limitations [4–9]. Hence, stabilization pretreatment of scrubber ash is essential to prevent heavy metals escaping into the environment and becoming a human health concern.

If the results of TCLP indicate heavy metal content of the ash to be beyond stipulated limit values, the ash ought to be subject to appropriate pretreatment. In Japan, for example, four pretreatment methods are utilized to treat scrubber ash: (1) cement solidification; (2) acid and other solvent treatment; (3) melting and solidification; and (4) chemical treatment

E-mail address: shaohwa@ms01.dahan.edu.tw.

[8,9]. The first method currently serves as the most common stabilization treatment. The heavy metals of scrubber ash are fixed in a cement structure during a hydration reaction. However, such solidification may deteriorate owing to moisture-absorbing compounds in the scrubber ash, resulting in diminished effectiveness of the solidification process and some dissolution of hazardous compounds. In the second method, water or acid solvent is applied to elute the heavy metals from the scrubber ash. The filter-cake remaining after leaching should be devoid of hazardous heavy metals. In this case, however, the leachate typically does not pass the effluent limit, for it includes large amounts of heavy metals which in turn must be conditioned with reagent by adding sodium sulfide or sodium hydroxide to form sulfide or hydroxide sludge. This process is not widely accepted for further complicated processes are needed to stabilize heavy metals in the sludge. The third method has proven to be the most reliable process where heavy metals are stabilized at a high temperature and the treated scrubber ash is suitable for use in construction materials; however, this approach has the disadvantages of relatively high treatment and equipment costs, and secondary pollution caused in the process. The last method involves forming insoluble solids with a liquid chelating reagent. It is simple and effective, but the organic chelating reagent is expensive and the stability of the subjective product with aging remains doubtful.

It is apparent from the above that chemical treatment could be an effective and economical treatment method for scrubber ash if the process can be modified to use an inorganic reagent instead of the organic chelating reagent. Tamaura et al. [10] presented a surface-coating stabilization method for treating laboratory wastewater in which the surfaces of the hazardous heavy metal waste were prevented from making direct contact with seawater, rainwater, and/or the drainage in landfill. The ferrite was formed on the surface of hazardous waste at 65 °C by partial oxidation of Fe^{2+} in solution. The resultant product was chemically stable and suitable for construction uses such as roadbed filler. Wang et al. [11] modified the method such that the ferrite was synthesized by mixing Fe^{2+} and Fe^{3+} at room temperature.

Based on the above discussions and considerations, the objectives of this study are to apply the ferrite process to stabilize scrubber ash and better understand the influence and amounts of Fe^{2+} and Fe^{3+} necessary in order to develop an economical and effective stabilization process for scrubber ash by chemical immobilization. To confirm our results, the stabilization of treated scrubber ash has been examined by multiple TCLP, XRD and SEM/EDS tests.

2. Materials and methods

2.1. Scrubber ash and stabilization reagents

(1) *Scrubber ash*: Three scrubber ash samples (samples A–C) used in this study were taken from MSW inciner-

ators in Taiwan. They were collected in bag filters after the flue gas had been treated by lime scrubbing.

(2) *Stabilization reagents*: Katayama Chemical Company of Japan supplied the powder reagents—the chemical formulas being $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, respectively.

2.2. Analytical methods

2.2.1. Analysis of X-ray fluorescence spectrometer (XRF)

The sample A was prepared by grinding the scrubber ash so that it could pass through a 200-mesh screen, and then pressing it into a cake. A Rigaku 3063 M XRF was then used to qualitatively analyze the chemical composition of the scrubber ash.

2.2.2. Analysis of XRD

The ground scrubber-ash cake (sample A) was placed in a holder forming the test sample. The holder was then placed in a Rigaku XRD machine with a copper target ($\lambda = 15.406 \text{ nm}$), a diffraction angle between 10° and 80° (2θ), and a scanning rate of $4^\circ/\text{min}$ was utilized to analyze the crystal phases of the scrubber ash.

2.2.3. Composition analyses of scrubber ash

For quantitative analyses of each of the procured elements, approximately 0.1 g of sample was placed into a pressure-resistant container lined with Teflon. Then regia and HF solution were added. The container was then placed in an oven for 2 h to dissolve the scrubber ash. A GBC 932 atomic absorption spectrometer (AAS) was used to quantify Ca, Si, Al, K, Fe, Na, Cr, Zn, Pb, Cu and Cd in the solution. The elements of S and Cl were analyzed by the National Science Council.

2.2.4. Analysis of the scrubber ash particle

A Shimadzu SA-200 laser diffraction particle size analyzer with alcohol as the suspension medium (refractive index of 1.70) was used to analyze scrubber-ash particle size.

2.2.5. SEM and EDS analyses

A Hitachi S-4100 ultra-high resolution SEM was used to observe the morphology of the samples. In turn, a Noran Voyager 2.0 EDS was used for composition analyses. The specimen was prepared by suspension in alcohol before being sprinkled onto an aluminum plate and then gilded in platinum by vacuum deposition.

2.2.6. TCLP test

Toxicity measurement procedures were carried out according to the TCLP testing guidelines specified in notification no. 0090 of the EPA of Taiwan. An ash sample (A) of 100 g was mixed with 21 of extraction liquid at $\text{pH} = 2.88 \pm 0.05$. The suspension was shaken for 18 h at

room temperature and filtered through glass fiber paper. The Cr, Zn, Pb, Cu and Cd elements were analyzed using an AAS.

2.2.7. Multiple TCLP tests

After completion of the stabilization experiment the scrubber ash was allowed to dry for 1 day. The finished products were then broken into finer particles of sizes less than 9 mm. These were used for toxicity tests. Nine TCLP tests were planned for the treated scrubber ash of sample A and the following hazardous elements Cr, Zn, Pb, Cu and Cd in the filtrate were later analyzed by AAS.

2.3. Stabilization experiments

Four hundred and fifty three grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 640 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ were dissolved, respectively, in distilled water and diluted to 1 l. The original concentrations of the mother solutions were 1.6 M; these solutions were then diluted to 0.4, 0.8 and 1.2 M for each reagent.

The identical concentrations of sulfate solutions were mixed, equal in volume, to give a mole ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ of 0.5. Thirty milliliters of mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution and 100 g of scrubber ash from sample A were stirred together for 10 min. The finished mud-like product was held at room temperature for a day before an initial TCLP test and multiple TCLP tests were carried out on the sample.

3. Results and discussion

3.1. Compositions of heavy metals in the scrubber ash

The grayish white powdery scrubber ash was settled in the bag filters after the acid flue gases of HCl and SO_x were treated with lime. The major heavy metals in scrubber ash samples (A–C) were analyzed, the contents are shown in Table 1. The heavy metals in three scrubber ash samples were comparatively low except Pb and Zn.

3.2. Size distribution of scrubber ash

An analysis of size distribution in the untreated scrubber ash is given in Table 2. The number of particle sizes larger than $149 \mu\text{m}$ represents about 5% of the scrubber ash sample A. A laser diffraction particle size analyzer was engaged to analyze the distribution of smaller particles with sizes less

Table 2

The distribution of particle sizes in the scrubber ash sample A

Particle size (mm)	wt.%	Accumulated wt.%
+4.76	0.32	0.32
−4.76 + 2.38	0.63	0.95
−2.38 + 1.41	0.91	1.86
−1.41 + 0.589	0.70	2.56
−0.589 + 0.295	0.96	3.52
−0.295 + 0.149	1.82	5.34
−0.149	94.66	100.00

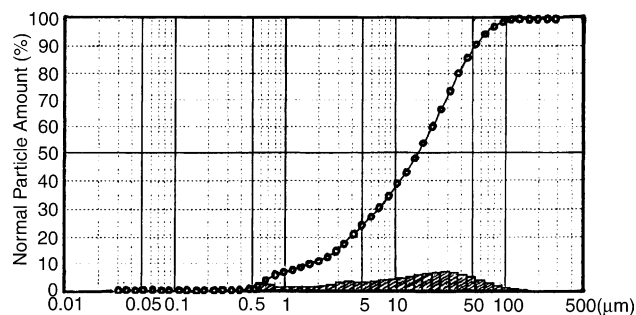


Fig. 1. Distribution of particle sizes less than $149 \mu\text{m}$ in the scrubber ash sample A.

than $149 \mu\text{m}$. The results are shown in Fig. 1, which indicates the size of most particles to be less than $50 \mu\text{m}$, and the average size of sample A is about $20 \mu\text{m}$.

3.3. XRF/EDS/XRD analyses of the scrubber ash

The qualitative analysis of scrubber ash sample A by XRF is shown in Fig. 2, where the composition of the scrubber ash is given as: Ca, Cl, K, S, Pb, Zn, Fe, Cu, and Si. EDS analyses of sample A–C revealed that the major elements were Ca, Cl and O. The quantities of Ca, Cl and O of ash samples were 26–40, 28–35, and 10–38%, respectively. Minor elements such as Si, K, Al, Na, Pb and Zn were present at about 0.2 to several percentage points, respectively, as shown in Table 1.

XRD patterns of untreated scrubber ash are shown in Fig. 3, revealing that the main crystal phases were CaClOH , $\text{CaCl}_2 \cdot \text{CaOH}_2 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{ClO})_2 \cdot 4\text{H}_2\text{O}$, NaCl, NaOH, KCl, CaCO_3 and C. These crystals were formed by reactions between HCl, SO_x and calcium oxide. The explanation for this is based on the fact that calcium oxide would effectively eliminate the chloride component from acid flue gas.

Table 1

The composition of scrubber ash

Sample	Elements (%)												
	Ca	Cl	S	Si	K	Al	Fe	Na	Zn ^a	Pb ^a	Cu ^a	Cr ^a	Cd ^a
A	25.7	32.3	6.9	1.2	2.7	0.7	0.5	1.0	11472	4729	754	666	269
B	30.0	28.6	8.1	3.4	1.9	1.3	1.3	1.3	4866	2234	1345	3213	101
C	23.7	35.7	4.8	6.3	1.6	1.5	1.6	0.8	8377	3157	1484	174	134

^a The elements are presented as mg/kg.

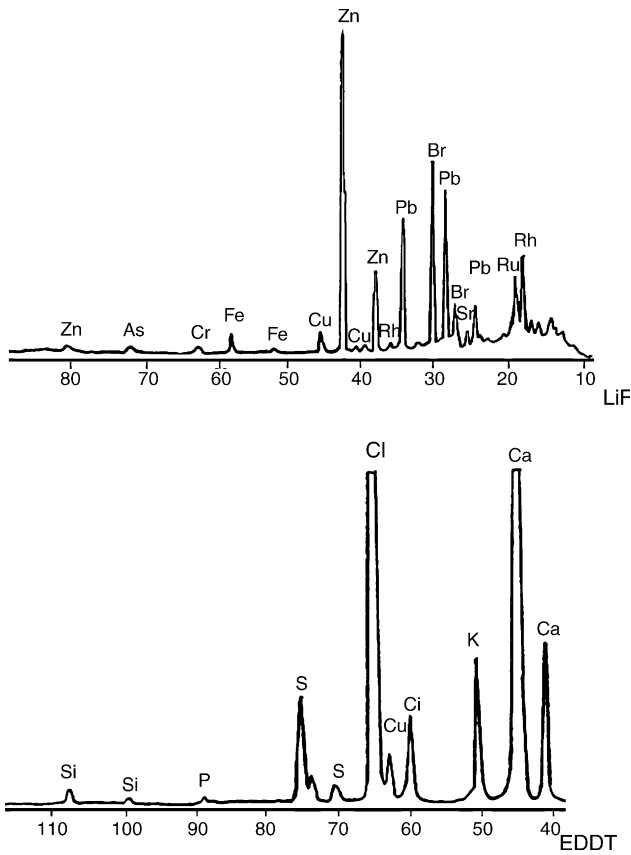


Fig. 2. XRF analysis results for the scrubber ash sample A.

3.4. Scrubber ash toxicity tests

During MSW incineration, the volatile and hazardous elements such as chloride compounds of Pb, Zn and Cd

Table 3
The results of TCLP tests for the untreated scrubber ash and treated products

Concentration of stabilization reagent FeSO ₄ ·7H ₂ O/Fe ₂ (SO ₄) ₃ ·xH ₂ O (M)	Analyzed elements (ppm)				
	Pb	Zn	Cu	Cd	Cr
0/0	87.2 ^a	5.7	0.4	0.1	0.8
0.4/0.4	46.2 ^a	3.2	0.4	0.1	0.7
0.8/0.8	36.6 ^a	2.8	0.4	0.1	0.7
1.2/1.2	8.6 ^a	1.0	0.3	0.1	0.6
1.6/1.6	2.5	0.3	0.2	0.1	0.5
Limit values	5.0	25.0	15.0	1.0	2.5

^a Data represent beyond limit value.

are condensed on to the small fine particle surfaces. The impact of scrubber ash on the environment was examined with TCLP testing with results of sample A being shown in Table 3. The results reveal that the concentration of Pb was 87.2 ppm, which exceeds the 5 ppm limit. On the other hand, other heavy metal contaminants such as Zn, Cu, Cr and Cd were so insignificant that they are not discussed in this paper.

3.5. Stabilization of scrubber ash

In general, scrubber ash from MSW is classified as specially controlled waste based on TCLP testing, which requires processing with specified pretreatments prior to landfill disposal. Immobilization of heavy metals in the matrix of stabilized products has been widely explored using ferrite coating, sodium silicate and sodium carbonate treatments [10,12,13]. Owing to the fact that the spinel structure of ferrite is highly stable, the ferrite process is frequently utilized in wastewater treatment to meet effluent limits or for the coating of hazardous particles to prevent dissolution of heavy metals from waste. However, the effectiveness of the

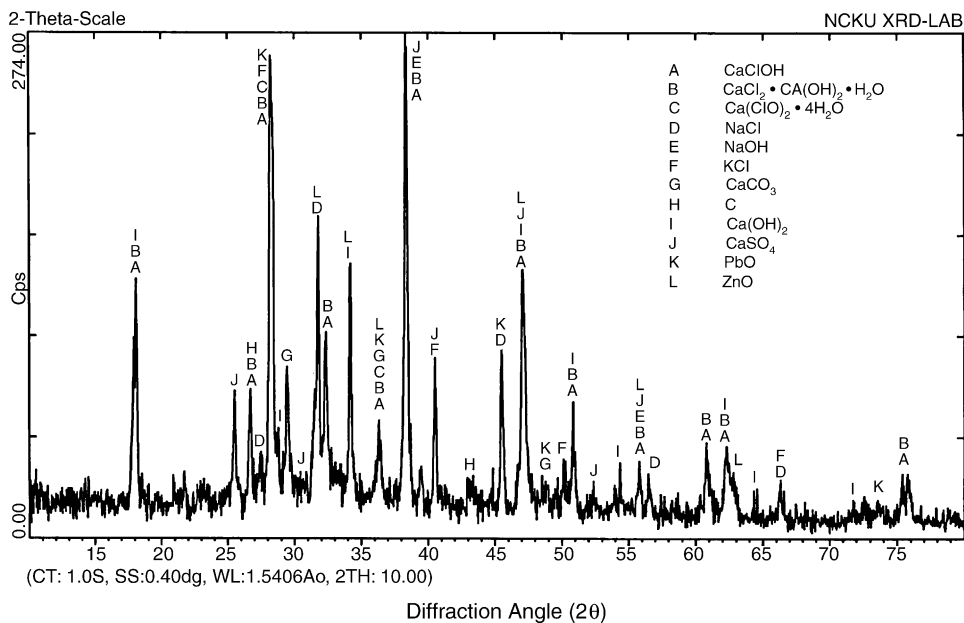


Fig. 3. XRD analysis results for the scrubber ash sample A.

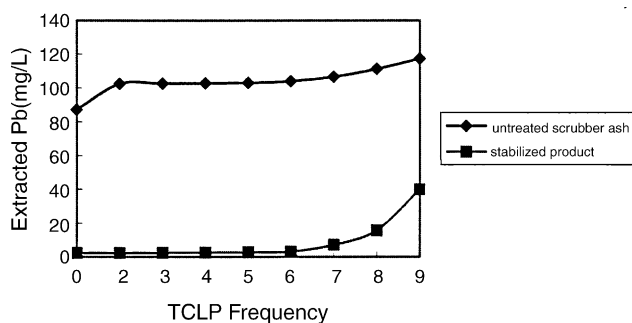


Fig. 4. Multiple TCLP test results for untreated scrubber ash sample A and stabilized product.

ferrite process is strictly influenced by $[\text{Fe}^{2+}]$, temperature, R -values ($2\text{OH}^-/\text{Fe}^{2+}$) and aeration conditions for proper MFe_2O_4 structures to be formed. This study was designed to improve the stabilization operation at room temperature in the ferrite process by using a mixed solution of Fe^{2+} and Fe^{3+} . When this solution is blended with scrubber ash it was expected that the hazardous materials would be stabilized effectively.

TCLP test results of the treated ash by the ferrite process are shown in Table 3, which reveals that the concentration of Pb in acetic acid leachate decreased from 87.2 to 2.5 ppm. The results also indicate that higher quantities of stabilization reagent in the stabilized product would lead to lower extractions of heavy metals under TCLP testing.

3.6. Multiple TCLP tests

The sample used for the nine TCLP tests was formed with 1.6 M ferrous/ferric sulfate during the stabilization experiment then mixed with acetic acid and corresponded to TCLP testing limits. Lead is examined here only because it exceeded the limit in the toxicity test of untreated scrubber ash. Obviously, during these TCLP tests, the total amount of Pb extracted from the tentative product in the leachate was lower than that from the untreated scrubber ash, as shown in Fig. 4. The extraction behavior of heavy metals in the untreated scrubber ash was different from that of the treated scrubber ash. In the former, most of the lead was extracted out during the first TCLP test, resulting in lower extraction in the follow-up tests. In the latter tests, only a little lead was extracted until the seventh TCLP test because of the stability of the structure formed in the treated scrubber ash.

Fig. 5 shows the accumulative weight loss of the untreated scrubber ash and treated scrubber ash as 70 and 50%, respectively, in the first TCLP test. This is due to the dissolution of soluble compounds such as NaCl, KCl and $\text{Ca}(\text{OH})_2$ in the scrubber ash as indicated in Fig. 3. In this case, not only soluble compounds, but also the heavy metals could be extracted from the untreated scrubber ash

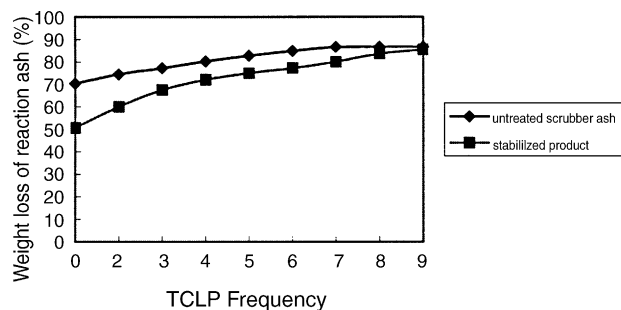


Fig. 5. Weight loss of untreated scrubber ash and stabilized product in multiple TCLP tests.

during the multiple TCLP tests. Naturally this resulted in the additional weight loss of the untreated scrubber ash compared to the treated scrubber ash. It is important to note as well that the accumulation of Pb in the acetic acid leachate of the treated scrubber ash was within TCLP test limits until the seventh test, when the stabilized structures of the treated scrubber ash began to breakdown allowing the lead to be extracted consequently exceeding the TCLP test limit. Eventually after the ninth test the weight loss of the treated scrubber ash matched that of the untreated scrubber ash most likely due to the destruction of stabilized structure.

Owing to significant amounts of calcium hydroxide being released, the pH value was higher (>10) in the filtrate of untreated scrubber ash during the multiple TCLP testing before the fourth test. By contrast, the pH of the filtrate of the treated scrubber ash was maintained at about 7 (see Fig. 6), indicating that the mixed reagents not only fixed the heavy metals with a stabilization structure in the treated scrubber ash, but also maintained a neutral pH value by decreasing the leaching of alkali compounds.

3.7. XRD analysis of the stabilized scrubber ash

The XRD patterns of stabilized scrubber ash are presented in Fig. 7. $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ was found in the diffraction peaks. This result may be due to significant quantities of calcium taking part in the spinel structure, replacing the Fe^{2+} sites, and

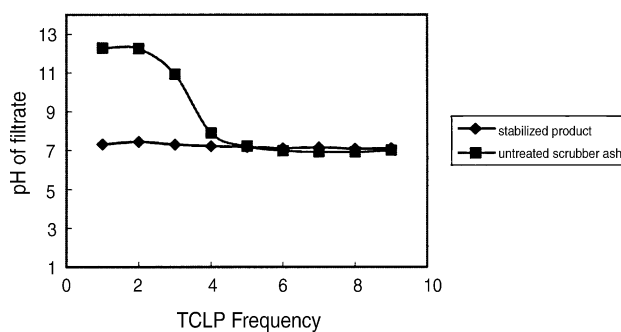


Fig. 6. Variations in pH value of acetic acid leachate from the scrubber ash and stabilized product in multiple TCLP tests.

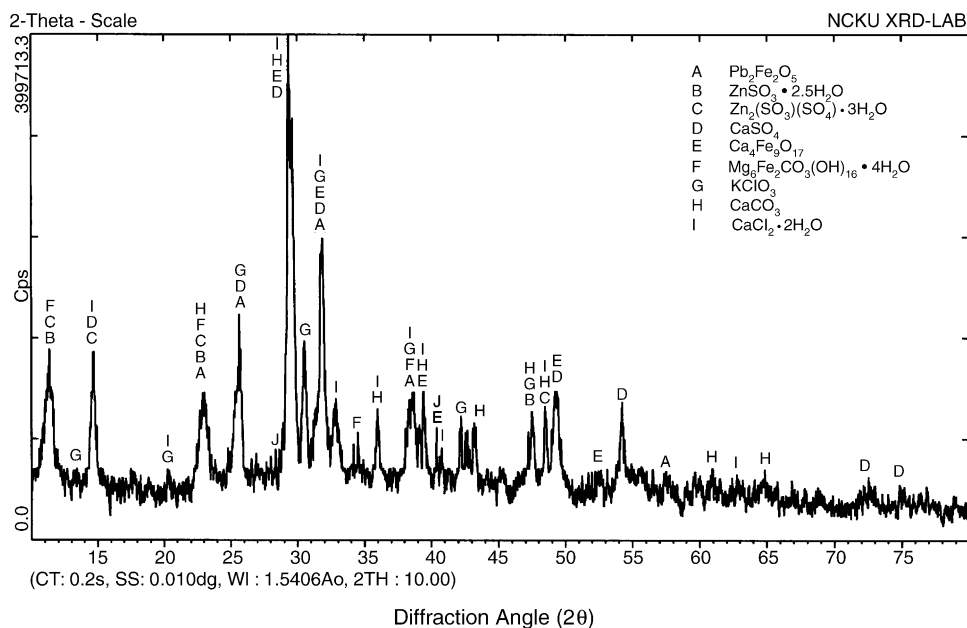


Fig. 7. XRD analysis results of the stabilized product.

giving rise to the formation of $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ in the stabilized scrubber ash. Gypsum was also formed through the effects of sulfate and calcium in the stabilization experiment. Thus, it must make some contribution to stabilize the scrubber ash.

3.8. SEM/EDS analyses of untreated and treated scrubber ash

The SEM micrograph of the untreated scrubber ash shows that the particle sizes of the ash were less than 10 μm , which

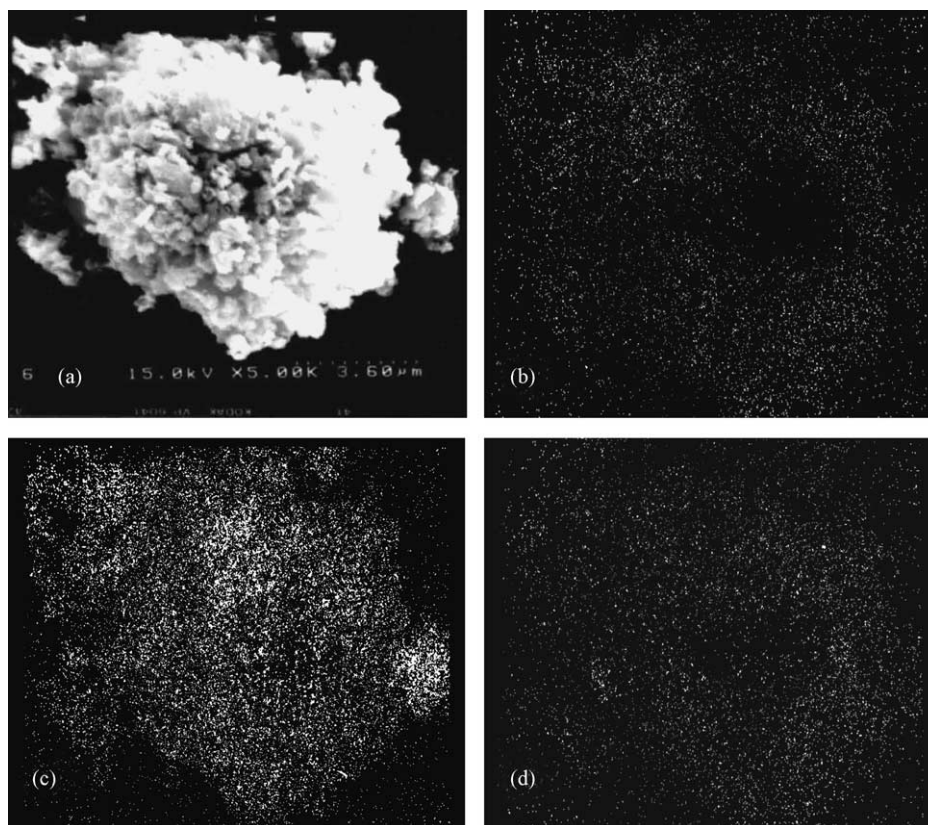


Fig. 8. SEM-EDS micrographs: (a) SEM image of the stabilized product; (b) Fe-mapping; (c) Ca-mapping; (d) O-mapping.

is in good agreement with the result of particle size analysis. The results of EDS-mapping analyses of the untreated scrubber ash also reveal that calcium and chloride were distributed over the particles uniformly, but silicon was rarely detected. It is assumed that the untreated scrubber ash was composed of CaClOH , $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$, and $\text{Ca}(\text{ClO})_2 \cdot 4\text{H}_2\text{O}$, in accordance with the results of the XRD analysis on the untreated scrubber ash.

The SEM micrograph and EDS-mapping analyses of the stabilized scrubber ash are shown in Fig. 8(a). The particle figure of the stabilized scrubber ash matched the result of Ca-mapping (Fig. 8(c)) proving calcium to be a major element in the treated scrubber ash. In other analyses, both results of Fe-mapping and O-mapping (Fig. 8(b) and (d)) show that their dot densities in figures were scattered in the same area. This might represent MFe_2O_4 structures forming on particle surfaces of the treated scrubber ash. However, the large amounts of calcium in the ash were part of the spinel structure resulting in the formation of $\text{Ca}_4\text{Fe}_9\text{O}_{17}$. The results of Fe-mapping and O-mapping indicate that the coating of $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ on the surfaces of the particles in the treated scrubber ash prevented the dissolution of heavy metals from the treated scrubber ash.

4. Conclusions

The MSWI scrubber ash used in this study was found to be of a diminutive particle size and significant amounts of calcium hydroxide were being released to cause pH values to exceed the regulation limit of 12.5 in the effluent. In addition, the extracted lead from untreated scrubber ash always exceeded the limit value of TCLP testing. Consequently, the MSWI scrubber ash used in this study ought to be classified as hazardous waste that requires specific pretreatments prior to landfill disposal.

The MSWI scrubber ash was treated with an 1.6M ferrous/ferric sulfate solution resulting in the formation of coating compounds such as MFe_2O_4 and $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ in the abundant presence of Ca on lead-contaminated waste surfaces, thus the treated scrubber ash could be stabilized and meet the regulation limits of TCLP testing.

Acknowledgements

The author thanks Professor Min-Shing Tsai for his advice, and Mr. Shing-Hui Chao for helping the experimental work.

References

- [1] N.B. Zhang, Introduction of incinerator development at Taiwan area A Engineering Scheme and Design of Waste Incinerator, vol. 1, Maw-Chang Ltd., Tainan, 1998, pp. 2–6 (in Chinese).
- [2] S.H. Hu, S.H. Chao, M.S. Tsai, Heavy metal stabilization of MSW fly ash with soluble silicate, *Bull. Chin. Inst. Min. Metall. Eng.* 43 (2001) 83 (in Chinese).
- [3] S.H. Hu, M.S. Tsai, The study on resources recovery from bottom ash of municipal waste by combustion, *Bull. Chin. Inst. Min. Metall. Eng.* 42 (1998) 83 (in Chinese).
- [4] A. Kida, Y. Noma, T. Imada, Chemical speciation and leaching properties of elements in municipal incinerator ashes, *Waste Manage.* 16 (1996) 527.
- [5] J.R. Conner, Fixation of metals, in: J.R. Conner (Ed.), *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinold Publisher, New York, 1990, pp. 74–75.
- [6] T. Mangialardi, A.E. Paolini, A. Poletti, P. Sirini, Optimization of the solidification/stabilization process of MSW fly ash in cementitious matrices, *J. Hazard. Mater.* 75 (1999) 53.
- [7] K.J. Hong, S. Tokunaga, T. Kajiuchi, Extraction of heavy metals from MSW incinerator fly ashes by chelating agents, *J. Hazard. Mater.* 75 (2000) 57.
- [8] Y. Zhao, L. Song, G. Li, Chemical stabilization of MSW incinerator fly ashes, *J. Hazard. Mater.* 95 (2002) 47.
- [9] T. Shimaoka, M. Hanashima, Behavior of stabilized fly ashes in solid waste landfills, *Waste Manage.* 16 (1996) 545.
- [10] Y. Tamaura, P.Q. Tu, S. Rojarayanont, H. Abe, Stabilization of hazardous materials into ferrite, *Water Sci. Technol.* 23 (1991) 399.
- [11] W. Wang, Z. Xu, J. Finch, Fundamental study of an ambient temperature ferrite process in the treatment of acid mine drainage, *Environ. Sci. Technol.* 30 (1996) 2604.
- [12] F.A. Lopez, A. Lopez-Delgado, J.L. Martin de Vidales, E. Vila, Synthesis of nanocrystalline zinc ferrite powders from sulphuric pickling waste water, *J. Alloys Comp.* 265 (1998) 291.
- [13] A. Lopez-Delgado, J.L. Martin de Vidales, E. Vila, F.A. Lopez, Synthesis of mixed ferrite with spinel-type structure from a stainless steelmaking solid waste, *J. Alloys Comp.* 281 (1998) 312.