Long-term Static Immersion Experiment on Leaching Behavior of Heavy Metals from Waste Printed Circuit Boards

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E-waste is growing at a speed of around 4% per year and has become the fastest growing waste stream in the industrialized world. Printed circuit boards (PCBs) are used in all electrical and electronic equipment (EEE) as well as the basis of the electronic industry. PCBs is making up of about 3% by weight of the total amount of electronic scrap. The PCBs have nearly 28% metallic content, which include Cu, Cd, Pb, Zn, Cr, Hg, Se and so on. These metals are hazardous and leachable, so waste PCBs have negative potential impacts on the environment and human health due to potential leaching of heavy metals by acid rain, meteoric water or groundwater into the environment with time. It is important to study the amount and leachability of heavy metals of waste PCBs.

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Abstract

Printed circuit boards (PCBs) are the main components of electrical and electronic equipment (EEE). Waste PCBs contain several kinds of heavy metals, including Cu, Pb and Zn. We characterize the leaching of heavy metals (Cu, Pb, Zn and Ni) from waste PCBs at a pH range of 3.0 to 5.6 using a novel approach based on batch pH-static leaching experiments in this work. Results indicate that the leaching behavior of Cu, Pb, Zn and Ni is strongly dependent on pH. Leaching behavior also varies with different pH values and leaching times. The maximum concentrations of Cu, Pb, Zn and Ni in leachate from waste PCBs were 335.00, 17.57, 2.40 and 2.33 mg·L^{-1}, respectively. The highest Pb, Ni, and Cu concentrations leached significantly exceeded the European Union waste-acceptance limit values with respect to inert waste landfills. The leaching of metals follow the shrinking core model with surface reaction control.

Keywords: printed circuit boards; heavy metal; leach; pH

Introduction

The amount of waste electrical and electronic equipment (WEEE) produced is extremely high, and this trend continually increases because of the heavy reliance on electrical and electronic equipment (EEE) despite their short lifespans. The generation of waste PCBs increases as global WEEE production expands because printed circuit boards (PCBs) are essential EEE components. The average annual growth rate of the worldwide PCB industry is 8.7%; however, China has higher rate of 14.4%[1]. Approximately 80% of the WEEE from the United States recycling industry is exported to Asia, and 90% of this amount is shipped to China[2]. Waste PCBs contain polyvinyl chloride plastic, brominated flame retardants, and toxic materials, including heavy metals. These metals comprise approximately 28% (copper: 10% to 20%; lead: 1% to 5%; nickel: 1% to 3%) of waste PCBs[3]. Waste PCBs also contain precious metals, the purity of which is over 10 times those of rich-content minerals[4]. Therefore, the recycling of metal in waste PCBs is a hot topic that has been discussed thoroughly over the past 10 years[3-8]. The lack of an appropriate management system and strict environmental regulations on WEEE in China causes the majority of WEEE to be processed in small, informal, and unqualified workshops. These workshops use basic methods, such as manual disassembly and open incineration, to recycle precious metals in waste PCBs for income-generation purposes. The processing procedures observed in these workshops lack pollution control measures; thus, groundwater and soil have been severely contaminated in areas such as Guiyu Town.

Several studies have investigated the actual pollution situation[9-16], and the data published in these reports show that heavy metals (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, and Pb) in rice and sediment exceed the relevant criterion. The lead levels in the blood of children are higher than those of children in neighboring areas. Various hazardous elements (Cu, Cd, Pb, Zn, Cr, Hg, and Se) in waste PCBs are non-biodegradable, and these elements tend to accumulate in living organisms, thus resulting in various diseases and disorders. Waste PCBs potentially cause the deterioration of groundwater and surface water quality if heavy metals are discharged at high concentrations. Thus, evaluating the fate and transportation of toxic metals in waste PCBs is necessary to identify remediation techniques that can control hazardous contamination.

However, the environmental risks posed by waste PCBs remain unclear. Laboratory leaching tests under normalized conditions can provide information on the environmental properties of waste PCBs to support decision-making in waste management.

Acid rain (AR) is a severe environmental issue in China because it affects approximately 40% of the country[17]. Yangtze River is one of the main areas affected by AR, where rainfall has a low pH value ranging from 4.0 to 3.5[18]. AR accelerates the leaching of elements from waste PCBs, thus causing these elements to migrate to surface waters. Some of these metals may be hazardous to people and natural biota, and the combination of AR and waste-PCB pollution results in new environmental problems.

The current study aims to investigate the chemical characteristics of heavy metals and their leaching behavior from waste PCBs. A long-term, static, immersion experiment with different pH values is designed, and the results are expected to provide helpful data regarding the potential risks imposed by metals from waste PCBs to the environment. This work also aims to provide policy makers with information for the planning of efficient environmental actions and control measures.

Materials and methods

Materials

Waste-PCB scrap samples were provided by Kaiyan Electron Co., Ltd, Nanjing, China. The end-of-life PCBs used in this study were heterogeneous and originated from PCs, telecommunication gadgets, and other electronic devices. PCBs were initially removed from electronic components and then smashed using a hammer mill. The samples were dried at 40 °C prior to the leaching experiments and passed through a < 2-mm stainless-steel sieve. The chemical compositions of the waste PCBs were determined using X-ray fluorescence spectrometry (XRF, ARL Corporation, Switzerland). The samples were digested with HNO_3-$HCLO_4$-HCl. The dried samples (1g) were put in Polytetrafluoroethylene (PTEE) Crucibles and 4:3:1 HNO_3-$HCLO_4$- HCl was added. The digested mixture were then diluted up to 50 mL with water and were saved for main metals analysis. Mineralogical analyses of the sample were conducted using X-ray diffractometer (XRD, ARL Corporation, Switzerland).

Leaching test

Leaching tests with six different pH values were conducted separately and simultaneously. Two parallel leaching tests were simultaneously conducted for each treatment in recognition of waste-PCB heterogeneity. First, 5 g of PCB particles were placed in a glass bottle containing 250 mL de-ionized water. The pH values of the de-ionized water were set to 3.00 ± 0.05, 3.50 ± 0.5, 4.00 ± 0.05, 4.50 ± 0.05, 5.00 ± 0.05, and 5.60 ± 0.05 with HNO_3 : H_2SO_4 (1:4) or NaOH solution according the AR pH values reported by Zhang et al. (2007)[17], and the treatments are referred to as AR1, AR2, AR3, AR4, AR5, and AR6, respectively. The particles were static and immersed in the acid solution for 90 d. 5 mL of the leachate was obtained without disturbing the immersed particles at 1 d to 2 d intervals. The pH value of the AR solution was deliberately increased during the process to account for the “alkalizing” effect of waste PCBs. Therefore, the pH value of the AR solution was similar to the initial pH value after a 5-mL sample with HNO_3 : H_2SO_4 (1:4) or NaOH solution was obtained.

Electrical conductivity (EC) and pH were determined shortly after the collection of each effluent fraction. Sub-samples were obtained and filtered through 0.45-µm membrane filters for chemical analysis. The clear filtrates were acidified with concentrated HNO_3 and then analyzed using atomic absorption spectrophotometry (AAS,SOLAAR M6, Thermo) to obtain solution concentrations of Cu, Pb, Zn and Ni. The Cu, Pb, Zn and Ni detection limits are 0.03, 0.07, 0.01 and 0.05 $mg\cdot L^{-1}$, respectively.

Morphology of waste PCBs

Scanning electron microscopy (SEM, S-3400N II, Hitachi, Japan) was used to determine the morphology of the waste PCB particles before and after the test.

Statistical analyses

The results presented are the arithmetic means with their corresponding standard deviations(SD). Differences between groups were tested for significance via ANOVA using Grapher 6.0. According to Tukey's multiple comparisons tests, $P<0.05$ and $P<0.01$ were considered significant and highly significant, respectively.

Results and discussion

Waste PCB particle morphology

Morphological observation via SEM is required to clearly understand the surface structure of waste PCBs. Fig. 1 depict SEM images of waste PCB particles. Waste PCB particles are categorized into two types: spherical particles and long bars. Energy-dispersive X-ray spectroscopy (EDX) (As shown in Fig.2) analyses show that the compositions of the spherical particles and long bars differ significantly; long bars are mainly composed of Cl, Br, Cu, K, C, and O, whereas spherical particles predominantly contain Si, Ca, K, C, and O. The morphology of waste PCBs varies from those of bottom or fly ash[19-21].

[Fig. 1 and Fig 2 were inserted here]

Characteristics of PCBs

Waste PCBs are visually characterized by white to gray color, which may be attributed to the high calcium hydroxide quantity.

The pH values of the PCBs samples were determined by adding de-ionized water at solid-liquid ratios of 1:5 and 1:30, followed by shaking for 10 min. The solution was left to stand for 20 min, and pH was measured using pH METER 6219. The pH values were 8.55 and 7.65, thus indicating that PCBs are alkaline materials. Several studies reported that bottom or fly ash is a strongly alkaline material[22-24] with a pH value of approximately either 12.0, 10.0, or 8.53, which is a value higher than that of waste PCBs.

The particle size distributions of the PCB samples were determined using a laser diffraction method (Malvern Master Sizer 2000). Over 80% of the particles are smaller than 222 μm, and the average particle size is 66.86 μm. X-ray diffraction (XRD) data for the samples is shown in Fig. 3. It shows the PCBs sample contain mainly metal Cu.

Waste-PCB particle compositions were measured using XRF. The analytical results are reported as metal oxides in Table 1. The main components are Si, Ca, Al. This composition is roughly similar to those of incinerator, fly, and bottom ash[22,24-29], as well as mineral processing waste[30,31]. Table 1 shows that waste PCBs contain harmful contents of heavy metals such as Cu, Pb, Zn and Ni. The digestion result showed Cu, Pb, Zn and Ni content at 7.57%, 0.43%, 0.52% and 0.3%, respectively. Cu may be the predominant metal element in PCBs. The compositions of Cu, Zn, and Pb in natural minerals are relatively low (e.g., Cu: 0.15% to 0.20%, Zn: 0.17% to 4.00%, Pb: 0.5% to 4.00%)[31]; however, the heavy metal contents of waste PCBs are higher than those of metal-enriched sewage sludge[32] and fly ash[20,26,27,29]. The physical and chemical properties of waste PCBs generally vary as a result of the effects of particle size and production technique.

[Fig. 3 was inserted here]

[Table 1 was inserted here]

Leaching behavior of heavy metals (Cu, Pb, Zn and Ni) with immersion time

Fig. 4 illustrate the relationships between the leaching contents of different heavy metals and leaching time. Two types of heavy metal leaching behavior as a function of time can be observed during the experiments. Type 1 (Cu and Ni) in the dissolution phase did not reach equilibrium during the experiment. This release pattern indicates either the strong binding of elements to PCBs or the slow dissolution of solid phases such as Fe-oxides. The change in Cu contents during the immersion process are shown in Figs. 5. Cu contents in AR1 and AR2 exhibit similar trends; they reach the peak at 80 d and then decrease slightly until the end of the experiment. By contrast, Cu contents in the leachate of the other four treatments (AR3, AR4, AR5, and AR6) slowly increased over time.

Type 2 (Pb and Zn) remains in a rapid dissolution phase until equilibrium is obtained. The two metal contents rapidly increased in the beginning stage until they reached their peaks, thus potentially representing the limited fraction of mobile metals in waste PCBs. The contents then decrease over time until a steady state is reached. The results show that the leaching of the four metals is initially controlled by the heavy metals of pastes on the surface, thus significantly increasing leaching rate. The compound of the four metals slowly transitions into a stable phase after the peak is reached. Alternately, the metals were absorbed on the oxides of iron, aluminum, and silicon. The leaching of the four metals from waste PCBs may be controlled by major elements (e.g., Ca and Si) and mineralogical compositions during the subsequent equilibrium phase, according to research on fly and bottom ash. The concentration-time patterns of the elements may be results of the dissolution/precipitation of minerals and sorption/desorption processes.

In conclusion, the contents of Cu and Zn in the leachate decreased with the increase in pH value during the leaching process. The results are similar to those of the majority of the research on bottom and fly ash. By contrast, the leachedcontents of Pb and Ni exhibited behavior different from those reported in previous studies[30,33-36]. Low pH resulted in strong metal leaching according to these studies. Pb contents at a plateau were approximately 2.81, 1.95, 1.58, 1.22, and 0.66 $mg \cdot L^{-1}$ in the following respective order: AR5 > AR4 > AR3 >AR2> AR1. This finding may be attributed to the decreased solubility of $PbSO_4$ in the leachate with the increase in pH value. Lee et al. (2002)[37] suggested that 80% of the Pb in the solution is removed via adsorption and co-deposition with Fe-hydrate when pH is less than 3.5. Kirby and Rimstidt (1994)[38] observed that carbonates are important in Pb phases if combined with municipal solid waste incineration (MSWI) bottom and fly ash. The Ni concentration in AR6 is higher than those in the other four pH treatments with the exception of AR1. This result suggests that the Ni pollutant is an area of concern.

Waste PCBs contain a certain amount of harmful heavy metals that can be leached by an AR solution, based on the analysis above. The leaching content of the four metals in the leachate (with an initial pH of 4.0 as an example) are compared with the European Union (EU) waste-acceptance limit values with respect to inert waste landfills to assess heavy metal contamination in the solution (Table 3. The highest Zn concentration is similar to the reference value, whereas the highest leaching levels of the other three metals (Cu, Pb and Ni) are significantly higher compared with the reference values. The ecotoxicity assessment of waste PCBs indicates that Cu and Pb are the most critical potential contaminants. Waste should be subjected to pretreatments prior to reuse.

[Fig. 4 was inserted here]

Variations in EC and pH

Variations in EC and pH during leaching are shown in Fig. 5. The six treatments display similar EC variation trends with leaching time, as shown in Fig. 5, EC initially increased rapidly, followed by a sudden decrease, and then steadily leveled off toward the end of the experiments. The EC curve shows that abundant soluble material was initially released into the solution. Other reactions subsequently occurred in the systems, which may have inhibited ionic activity in the solution. Leached pH value increased over the leaching period, which demonstrates the significant effect of waste-PCB alkalinity on the chemistry of the leaching solution. pH variation is mainly attributed to the strong buffering capacity of the waste PCBs coupled with the large Ca and Mg quantities.

[Fig. 5 was inserted here]

Leaching kinetics

For a liquid/solid reaction system, the shrinking core model considers that the leaching process and its rate is generally controlled either by the diffusion of reactant through the liquid film, or through a solid product layer, or by rate of the chemical reaction at the surface of the core of unreacted particles or a mixed of diffusion and chemical reactions. The rate of the process is controlled by the slowest of these sequential steps.The shrinking core model can be respectively illustrated by Eqs. (1)–(3) as follows[8,39-41].

$$K_1 t = 1-(1-\alpha)^{1/3} \quad (1)$$

$$K_2 t = 1-(2/3)\alpha-(1-\alpha)^{2/3} \quad (2)$$

$$K_3 t = (1/3)\ln(1-\alpha)+(1-\alpha)^{-1/3}-1 \quad (3)$$

Where a is leaching efficiency of metals, k_1, k_2, k_3 are rate constants, and t is treatment time. As can be seen from Eqs. (1)-(3), when the process is controlled by chemical reaction, internal diffusion, both the interface transfer and internal diffusion. For the kinetics analysis of leaching process in the present study, these models were assessed by using correlation coefficients in Table 2. As can be observed from Table2, Eq. (1) fitted better comparing with the other two Eqs, therefor,the chemical reaction is the rate controlling step.

[Table 2 were inserted here]

Total heavy metal losses

The analysis of high heavy metal loss during leaching could directly reflect the leaching strength of heavy metals. The highest heavy-metal in each treatment during leaching are shown in Fig. 6. Approximately 96%, 88%, and 75% of the initial Cu and Zn contents were leached from waste PCBs in the AR1 treatment. The high contents of dissolved Cu and Zn are attributed to weak metal retention on the surface of the PCBs. Heavy metal mobilization is widely recognized as dependent on the association form in the solid phase to which the metals are bound during chemical reactions[42]. Aside from pH, metal release is also affected by geochemical association and distribution in coal fly ash and long-term, environmentally relevant conditions[43]. Metal (Cu and Zn) loss is suddenly reduced when pH is increased. This phenomenon is attributed to the precipitation of metal as hydroxides. Lower available Ni and Pb concentrations are observed compared with the initial total metal amount. The highest Pb and Ni concentrations remain higher than the EU limit values even when their potential availability decreases, although only approximately 30% of Ni and Pb in the waste PCB samples are considered labile (mobile) forms. Therefore, the trace metals leaching from waste PCBs should be considered in any waste-management scenario.

[Fig. 6 was inserted here]

[Table 4 was inserted here]

Comparison of waste PCB morphology in the initial stage and after 90 d of immersion

SEM images of PCB particles that were immersed for 90 d in the AR1 treatment were obtained. The immersed particles were separated from the aqueous solution by centrifugation and then dried at 60℃ prior to scanning. The SEM images (Fig. 7 and Fig. 8) show that PCB powder immersed in AR1 is rougher than the initial PCB powder (Fig. 1) and exhibits increased aggregation. The long poles are broken into shorter poles potentially because of the pH effect. Small amounts of Cu and Fe were detected in the spherical particles of the PCBs immersed in AR1 treatment when the EDX of these particles were compared with that of the initial PCBs. Cl should have dissolved into the solution. Therefore, the results clearly indicate that spherical particles become evident at low pH because of soluble metal dissolution.

Extensive databases on waste PCB characteristics and heavy metal leaching are not available. Si, Al, Ca, and Fe are predominant components of waste PCBs, and these components also comprise other solid wastes (e.g., bottom and fly ash). Variations in the behavior of these metal elements can be attributed to different factors. Numerous studies on the behavior of trace metals focused on the leaching behavior of major and trace elements obtained from bottom ash, fly ash, and slag tailing. Previous research also focused on the factors inherent to the nature of bottom ash (e.g., waste particle morphology, chemical and physical properties of wastes) and on external factors related to environmental conditions (e.g., rainwater, temperature change, and acid). Few researchers introduced geochemical knowledge with which to characterize waste because waste materials were viewed as mineral assemblages similar to rocks and soils[34,44,45].

Several authors concluded that solubility and adsorption phenomena control leachate composition and that different mineralogical transformations occur over time with environmental exposure. Few studies proposed that dissolution/precipitation reactions or sorption processes control the leaching of major elements and contaminants from waste materials, such as MSWI bottom ash, coal fly ash, and solid wastes from oil shale[34,38]. Amorphous iron and aluminum hydroxides are known to serve important functions in trace element retention in the aforementioned ashes. These results show that a combination of dissolution/precipitation, sorption, and complexation reactions is required to control heavy metal solubility[37].

Ca minerals in MSWI bottom ash mainly control leachate pH, which has consequently been identified as a major parameter that controls the leaching of numerous elements. Iron precipitation is also favorable in the co-precipitation and/or sorption of other metals . The effect of pH on the leaching of metals (especially Cu and Zn) from waste PCBs concurs with previous studies, which report that the leachability of cationic metals, such as Cd, Cr, Zn, Pb, Hg, and Ag, increases with the decrease in pH[22,46-48]. pH is a key parameter that determines heavy metal mobility in soils, sediments, and waste materials[47]. It affects the solubility of these metals and also influences the formation of metal hydrolysates. Hydrous ferric oxide and amorphous aluminum hydroxide sorption databases have been used previously to model the leaching of trace elements from incineration residues. The effect of carbonation on the leaching toxicity of these samples was also intensively investigated[34,48-50]. Thus, understanding the factors affecting metal dissolution in waste PCBs is critical to the prediction of the potential effects of this process on the environment.

Major elements (Ca, Mg, Na, K, Cl, SO_4, CO_3, NO_3, and Cl) must be studied before the leaching of metal elements can be completely understood, based on the analysis above. Geochemical modeling can be used with conventional petrographical and/or advanced micro-analytical techniques and quantitative mineralogical analyses (SEM, XRD, and X-ray powder diffraction) to investigate the chemical composition of waste PCBs, leaching behavior, and the leaching mechanism of the heavy metals with respect to waste PCBs both in the laboratory and the field. Leaching tests must be conducted according to standardized methods to determine the hazards of waste PCBs. For instance, either pH-static leaching experiments, column tests, toxicity characteristic leaching procedures, or single and sequential chemical extraction can be employed. The various sources of waste PCBs and different particle sizes should be carefully selected.

[Fig. 7 and Fig. 8 were inserted here]

Conclusions

The following conclusions are reached and suggestions are provided based on the results for subsequent treatment:

1. Total Cu, Zn, Pb and Ni contents of waste PCBs are higher than those of bottom and fly ash.
2. Four trace elements, namely, Cu, Pb, Zn and Ni are released differently according to various pH values and durations. Cu was released slowly during immersion time. The leaching of metals follow the shrinking core model with surface reaction control.

3. The highest leaching concentrations of Cu, Pb and Ni at a pH of 4.0 are 335, 17.35, and 2.33 $mg \cdot L^{-1}$, respectively. These values exceeded the EU waste-acceptance limit values with respect to inert waste landfills. Therefore, PCBs can be considered a potential source of the heavy metal contamination of soil and water resources. Thus, the development of proper waste PCB treatment and disposal is urgent and necessary. The maximum loss percentages of the metals suggested that Zn and Cu can be leached easily.

4. All four metals were pH-dependent, with the exception of Ni and Pb. The leaching levels of the other two metals increased with pH reduction. Thus, pH value is an important factor that affects heavy metal solubility in waste PCBs.

5. The SEM and EDX of the metals that were immersed for 90 d displayed shorter bars and more spherical assemblies compared with those of the metals at the initial stage.

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Figure Captions

Fig. 1. SEM micrographs of initial waste PCBs with different magnifications: (a) 500× and (b) 2000×

Fig. 2. SEM micrographs and corresponding EDX of initial waste PCBs with 500×magnification

Fig.3 X-ray diffraction (XRD) data of the sample.

Fig. 4. Dynamic changes of leachate Cu, Pb, Zn, Ni contents for all treatments with leaching time

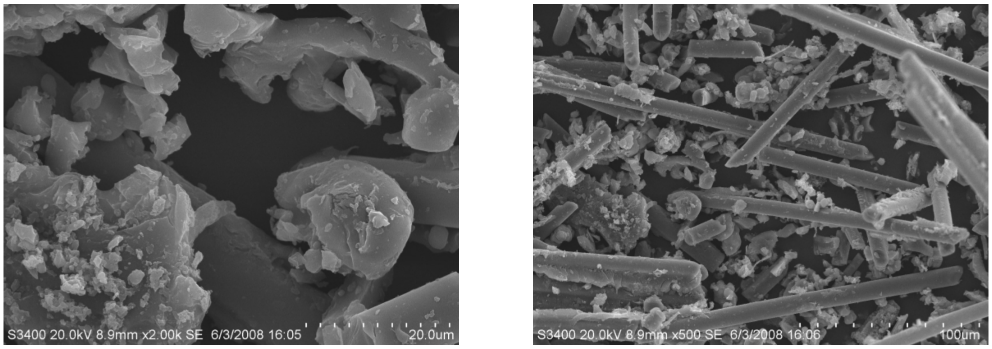
Fig. 5 Variation of electric conductivity and pH in leaching experiments

Fig. 6. the highest leaching contents of heavy metals

Fig. 7. SEM micrographs of waste PCBs after 90 d of immersion at pH 3 with different magnifications: (a)

500× and (b) 2000×

Fig.8. SEM and the corresponding EDX spectra of waste PCBs after 90 d of immersion at pH 3.0 with 500× magnification



a b

Fig. 1. SEM micrographs of initial waster PCBs with different magnification: (a) 500× and (b) 2000×

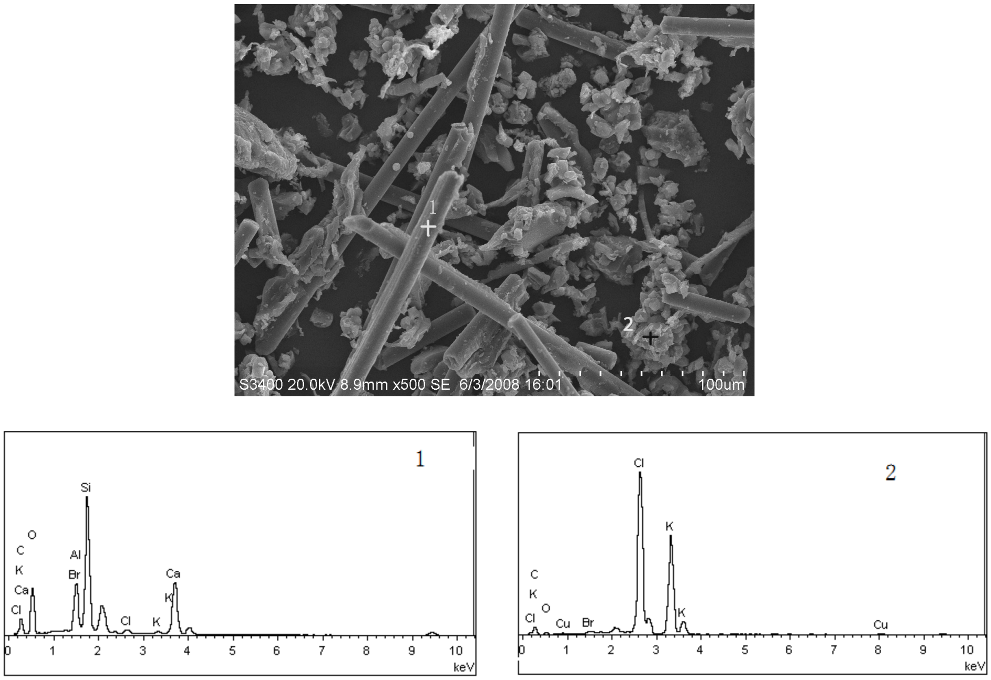


Fig. 2. SEM micrographs and corresponding EDX of initial waste PCBs with 500×magnification

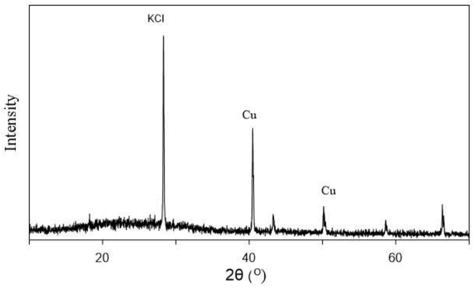


Fig.3. X-ray diffraction (XRD) data of the sample.

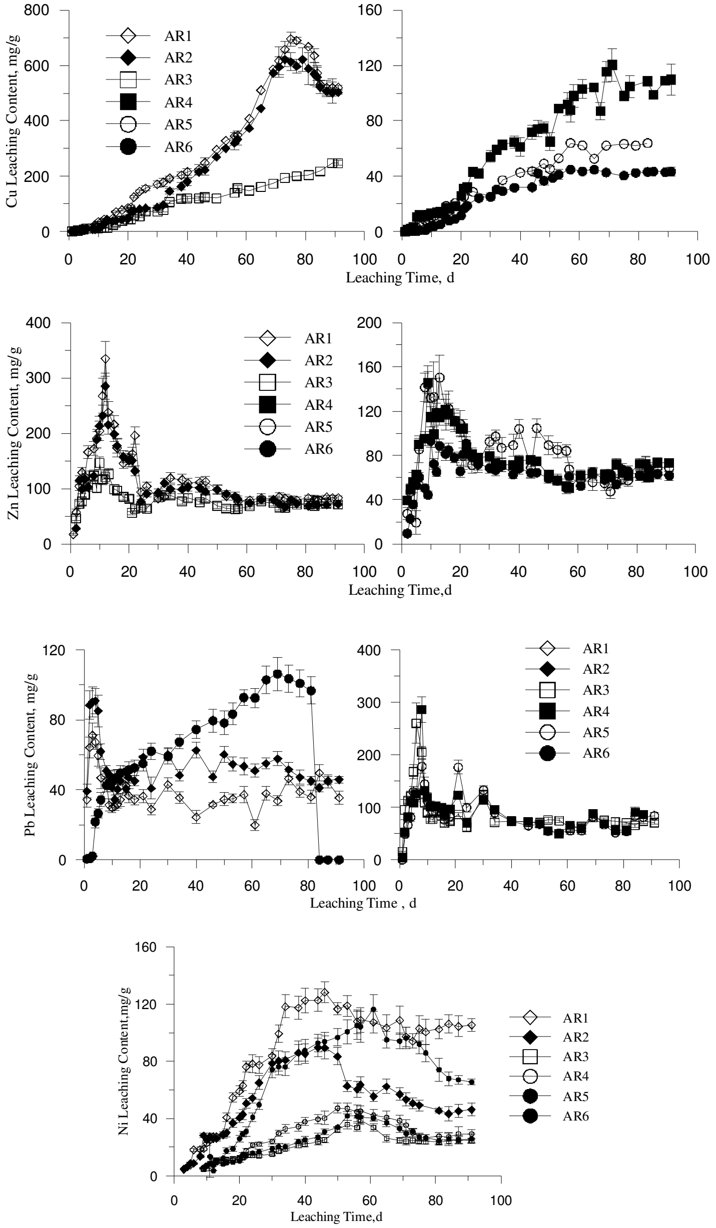


Fig. 4. Dynamic changes of leachate Cu, Pb, Zn, Ni contents for all treatments with leaching time. Note: values represent means±SD of three replicates, $C_0 = C \times V \div W \div P$,Where C_0 represents metal leaching content, mg/g; C represents leaching concentration, mg/L; V represents leaching volume, L;W represents waste PCBs sample weight, g; P represents metal of waste PCBs content, %.

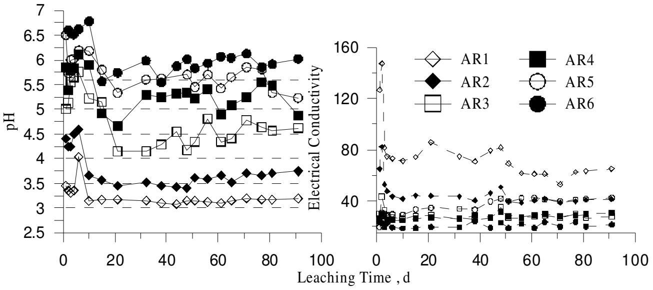


Fig.5. Variation of electrical conductivity and pH in leaching experiments.

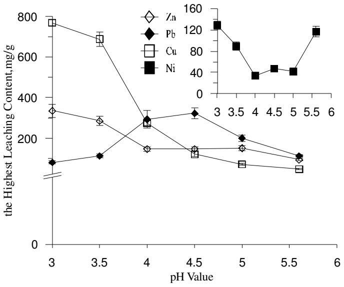
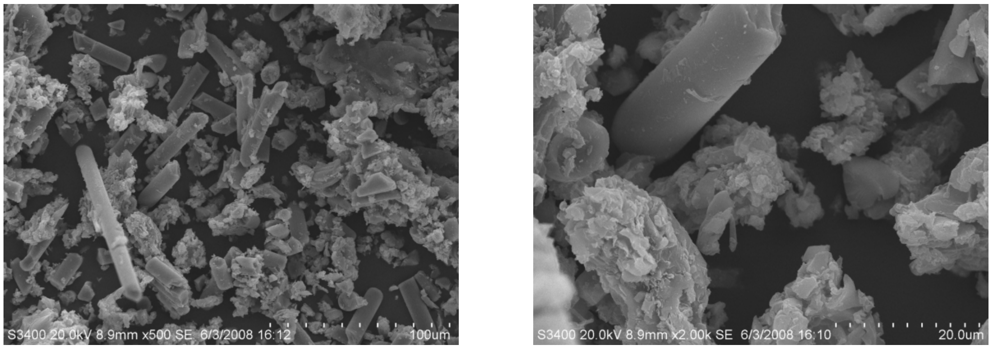


Fig. 6. The highest leaching contents of heavy metals. Values represent means±SD of three replicates



a b

Fig.7 SEM micrographs of waster PCBs after 90-day immersed with 3.0 with different magnification:

(a) 500× and (b) 2000×

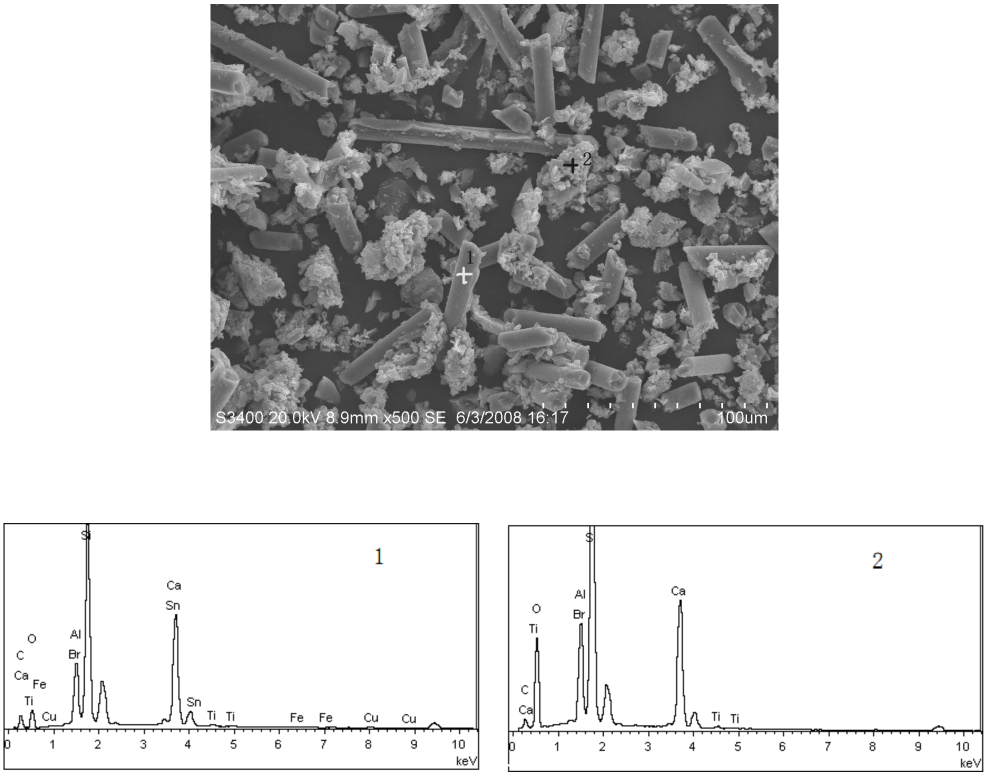


Fig.8 Scanning electron micrographs and corresponding energy dispersive X-ray spectra of waste PCBs after 90-day immersed with 3.0 with 500×

Table 1 Chemical composition of waste PCBs powder

%	SiO_2	CaO	Al_2O_3	Br	P_2O_5	CuO	PbO	SnO_2	Cl	Al_2O_3
	44.2	14.2	7.32	5.54	1.74	7.93	0.41	0.79	0.11	0.50
mg/kg	ZnO	NiO	MnO	SrO	K_2O	Fe_2O_3	SO_3			
	0.06	0.12	0.09	0.01	0.04	0.10	0.20			

Table 2 Coefficient of metal leached equations with different pH

Metal	Equation	AR1	AR2	AR3	AR4	AR5
Cu	Eq.1	0.900	0.867	0.987	0.940	0.956
	Eq.2	0.662	0.610	0.930	0.901	0.920
	Eq.3	0.570	0.529	0.882	0.907	0.941
Ni	Eq.1	0.973	0.962	0.963	0.970	0.977
	Eq.2	0.935	0.938	0.939	0.952	0.937
	Eq.3	0.931	0.935	0.952	0.935	0.934
Zn	Eq.1	0.928	0.879	0.740	0.730	0.801
	Eq.2	0.758	0.763	0.698	0.634	0.714
	Eq.3	0.969	0.831	0.690	0.620	0.708
Pb	Eq.1	0.889	0.784	0.898	0.861	0.949
	Eq.2	0.922	0.798	0.753	0.668	0.908
	Eq.3	0.924	0.798	0.905	0.643	0.891

$p<0.01$

Table3 Comparison between leaching concentrations of Cu, Pb, Zn and Ni (pH = 4.0) in this study the EU limit values for acceptance of waste at inert waste landfills ($mg \cdot L^{-1}$)

	Cu	Pb	Zn	Ni
Highest leaching level	335.0	17.57	2.47	2.33
Landfilling EU inert waste	0.9	0.2	2	0.2