



Mineralogy and heavy metal leachability of magnetic fractions separated from some Chinese coal fly ashes

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ABSTRACT

Magnetic fractions (MFs) in fly ashes from eight coal-burning power plants were extracted by magnetic separation procedure. Their mineralogy and potential leachability of heavy metals were analyzed using rock magnetism, X-ray diffraction (XRD), scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM/EDX) and leaching procedures (toxicity characteristics leaching procedure by the United States Environmental Protection Agency, TCLP, and gastric juice simulation test, GJST). Results show that the MFs in the fly ashes range between 2.2 and 16.3 wt%, and are generally composed of magnetite, hematite, quartz and mullite. Thermomagnetic analysis and SEM/EDX indicate that the main magnetic carrier magnetite is substituted with small amounts of impure ions, and its structures are featured by rough, dendritic and granular iron spherules. The MFs are found to be rich in Fe, Mn, Cr, Cu, Cd and Pb. Compared with the non-magnetic fractions (NMFs), the MFs have about 5 times higher iron, and 1.6 times higher Mn, Cr, Cu and Cd concentrations. The TCLP test shows that the TCLP-extractable Cr, Cu, and Pb concentrations in the MFs are higher than those in the NMFs, while the TCLP-extractable Cd concentration in the MFs and NMFs is below the detection limit (<0.1 mg/L). The GJST-extractable Cd, Cr, Cu, and Pb concentrations in the MFs are higher those in the NMFs. No significant difference in the leachability ratio of Cr, Cu and Pb with TCLP and GJST is found in the MFs and NMFs. However, the GJST test showed that Pb has higher leachability in MFs than that in NMFs. The leachability ratio of heavy metals has an order of Cu > Cr > Pb > Cd. The heavy metals of fly ashes have a great potential to be released into the environment under acid environment.

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1. Introduction

Fly ashes, a product of high temperature combustion of coal in thermal power plants, are known as an important source for the atmospheric particulate pollutants [1,2]. The tiny fly ash particulates spread through airborne processes and are deposited over a wide area. It has been reported that fly ashes contain significant amounts of magnetic components [3–6], and that such magnetic minerals result in a significant magnetic enhancement in soils, sediments and tree leaves around the emission sources of fly ashes [7–11]. Previous researches [5–11] have shown that magnetic particles in the fly ashes are mainly composed of magnetite, which could also be the most important source of anthropogenic magnetic particles in soils, sediments and tree leaves in the fly ash-affected areas. Environmental magnetic response to the accumulation of magnetic particles from fly ashes can be easily determined by monitoring magnetic susceptibility. Therefore, the magnetic properties of soils,

sediments and tree leaves can be used as an identification of the fly ashes emissions. Previous reports [7,9,11] show that magnetic measurement technique is a powerful tool for tracing and mapping atmospheric pollution of fly ashes. For example, magnetic measurements [7,9,12] have been successfully used to map the spatial distribution of fly ashes deposition and translocation in soil profile. Wide regional scale magnetic mapping of fly ash pollution has been done in England, Poland, and Austria [13–15].

Release of heavy metals from fly ashes is another environmental concern associated with the land disposal and agronomic utilization of fly ashes. This stimulated studies on the element composition of fly ashes and element release from fly ashes. A number of publications [16–20] have reported that the fly ashes contain many potential toxic heavy metal elements, including Pb, Zn, Cd, Ni, As and Co, which could contaminate soils, surface water and even groundwater. Most fly ashes are primarily composed of aluminosilicate materials and iron oxide phases. In general, the iron oxide phases were believed to be less resistant to the leaching processes than the aluminosilicate one. Kukier et al. [6] simply used magnet to separate magnetic and non-magnetic fractions of the fly ashes and determined that the concentrations of Co, Ni, and

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Fig. 1. Sketch map of the location of eight coal-burning power plants for sample collection.

Mn were 2–4 times higher in the magnetic fraction than in the non-magnetic fractions. Hulett et al. [19] reported that the concentrations of the first row transition metals were about ten-fold higher in the magnetic fraction than in the non-magnetic fraction of fly ashes, suggesting that the removal of the magnetic fractions could effectively reduce the release of these metals from fly ashes. On the other hand, the magnetic fractions of fly ashes have been found some applications in industries such as producing of heavy suspensions in ore and coal preparation plants, production of ferrosilicon or substitute for commercial magnetite, and dense concretes with an application in shielding radioactive materials [1,4,5]. Therefore, information on the differences in element composition and solubility of elements in the magnetic and non-magnetic fractions is important for safe disposal and multi-utilization of fly ashes [5,6]. It is even more relevant for agronomic utilization, environmental magnetic monitoring and the use of fly ashes for adsorbent of pollutants.

The bulk content of heavy metals in fly ashes from various sources has been determined [1,5,6,17,19,21,22]. These data give information concerning possibility of pollution from the release of heavy metals in fly ashes, but there is no sufficient information for estimating effects of heavy metals in fly ashes on environment and health. In other words, the behavior of various heavy metals in the environments, such as bioavailability and toxicity, cannot be reliably predicted on the basis of their total concentration. Therefore, many leaching procedures have been developed to simulate the leaching processes of hazardous wastes in landfills or natural environments in order to evaluate the risk of human health of tested wastes [23–30]. As a standard leaching test the toxicity characteristics leaching procedure (TCLP) from the US Environmental Protection Agency (US EPA) [23] is often used to determine if a material or polluted site present a threat to the environment and humans. Recently, Mercier et al. [31] developed a simple and fast screening test (gastric juice simulation test, GJST) to detect soils polluted by lead. The GJST proved to be a better estimator of lead bioaccessibility in the gastrointestinal tract. Some authors have used the TCLP test to examine leaching characteristics of a variety of bulk fly ashes [20,25,29], but these studies have not reported the leaching of different component in fly ashes. Published data concerning GJST leaching test of fly ashes is scant.

Although minerals and chemical composition of fly ashes have been well determined in previous literature, it is still necessary to characterize the magnetic phases in fly ashes in detail for identifying the source of magnetic pollution of fly ashes on soils, sediments, and tree leaves. Information on composition and solubility of heavy metal elements in the magnetic fraction is also helpful for safe disposal of fly ashes. The objective of this investigation was to provide

the basic magnetic property and chemical composition of magnetic fractions of the fly ashes from different thermoelectric power plants using rock magnetism, XRD and SEM/EDX analyses. The potential leachability of heavy metals in magnetic and non-magnetic fractions of fly ashes is also studied using the TCLP and GJST leaching tests.

2. Materials and methods

2.1. Magnetic separation procedure

Fly ash samples were collected from 8 coal-burning power plants in eastern China, as indicated in Fig. 1. Magnetic fractions (MFs) in the fly ashes were extracted according to the following procedure. The fly ashes were dispersed in deionized water in solid/liquid (S/L) ratio of 1:10. The resulting slurry was formed in a continuous-loop flow by a pump, and the magnetic particles were extracted out of the fly ashes by a high-gradient magnet. This procedure was run repeatedly until no more magnetic particles were attracted to the magnet. The separated magnetic and non-magnetic fractions were dried at 50–60 °C and then weighed. Magnetic susceptibility values of both the magnetic fractions and the residue (hereafter called non-magnetic fractions, NMFs) were measured. The extraction efficiency was calculated based on the change in magnetic susceptibility values before and after the separation.

2.2. Rock magnetism

Different rock-magnetic methods were used to characterize and identify the magnetic minerals in fly ashes. The low field magnetic susceptibility at 0.47 and 4.7 kHz, respectively, was determined using a Bartington MS2 meter (Bartington Ltd., UK) [32] and isothermal remanent magnetisation (IRM) at 1000 mT (defined as saturation isothermal remanent magnetisation, SIRM) using a Molspin fluxgate magnetometer (Molspin Ltd., UK). Magnetic susceptibility value provides an indication of the concentration within the sample of strongly magnetic ferrimagnets, such as magnetite. SIRM values reflect contributions from all remanence-carrying minerals, including the ferrimagnets and also weakly magnetic minerals such as hematite and goethite. Frequency-dependent magnetic susceptibility was defined as $\chi_{fd}(\%) = [(\chi_{lf} - \chi_{hf}) / \chi_{lf}] \times 100$, where χ_{lf} and χ_{hf} represent susceptibility values at 0.47 and 4.7 kHz, respectively [32]. Magnetic susceptibility versus temperature curve was obtained by measuring continuously from room temperature to 700 °C and back to room temperature in a KLY 3 Kappa bridge equipped with a CS3 high temperature attachment (AGICO, Brno, Czech Republic).

2.3. XRD and SEM/EDX

X-ray diffraction (XRD) patterns of the magnetic fractions were obtained on a Rigaku D/Max 2550 PC diffractometer with Cu K α radiation (40 kV, 300 mA) (Rigaku Corporation, Japan) by scanning from 2° to 80° at 0.2° θ per min. Magnetic fraction samples were gold-coated for scanning electron microscope (SEM) observation with qualitative EDX analysis. SEM observation was done on a Hitachi S-570 SEM with electron probe for X-ray microanalysis (EDX) at an acceleration voltage of 25 kV. Elemental spectra of the magnetic particles were obtained using a Hitachi S-570 SEM combined with a WD-8 energy-dispersive spectrometer. Qualitative and quantitative analyses of the elemental spectra were performed using a WD-5 software program.

2.4. Total metal analyses

The magnetic fractions (MFs), non-magnetic fractions (NMFs) samples and bulk fly ashes were digested with a mixed solution of the concentrated acids of HNO₃–HF–HClO₄ in a microwave oven (Mars-5, CEM Company, USA) according to the standard method [33]. After digestion, the suspension was cooled and diluted with 10–15 mL of deionized water and filtered. The filtrate was diluted to 50 mL with deionized water and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for Na, Mg, K, Ca, Fe, Cr, Mn, Ni, Cu, Zn, Cd, and Pb.

2.5. TCLP and GJST tests

The toxicity characteristics leaching procedure (TCLP) of the United States Environmental Protection Agency is commonly used to assess pollutant leachability [23]. The gastric juice simulation test (GJST) is a better estimator of heavy metal bioaccessibility in the gastrointestinal tract [31]. In our study, the TCLP and GJST tests are used to evaluate the potential leachability of heavy metals (Cd, Cr, Cu and Pb) in MFs and NMFs. The TCLP test was conducted according to US EPA method 1311 [23]. Five gram samples were added to 100 mL extracting solution and shaken for 18 h at room temperature. The pH of extracting solution was adjusted to 4.93 using 0.1 mol/L acetate buffer containing 63.4 mL of 1.0 mol/L NaOH and 5.7 mL acetic acid (CH₃COOH) in 1 L of deionized water. Suspensions were filtered through a 0.45- μ m filter paper and preserved by adding concentrated HNO₃ until the pH of the filtrate was below 2.

The GJST test was carried out according to the experimental protocol described by Mercier et al. [31]. In brief, 6 mL of acetic acid was added to 8 L of deionized water heated to 37 °C in a water bath. The samples were placed in the bottle with the extraction solution in a liquid/solid ratio of 22.2. Concentrated HCl was added over a 20-min period to obtain a pH of approximately 6. The samples were agitated for 20 min on an agitator appropriate for the TCLP. The samples were returned to the water bath and were acidified with HCl to a pH 4 of over another 20-min period. These operations were repeated for a pH value of 2.5 and 2. At the end of the extraction, the samples were

Table 1
Magnetic properties and mass of MFs in fly ashes.

Samples	χ If (10^{-8} m ³ /kg)	SIRM (10^{-4} Am ² /kg)	Mass of MFs (%)
1	1703.3	254.4	16.3
2	1619.8	247.0	13.7
3	490.3	146.7	2.4
4	561.3	153.0	2.2
5	481.3	145.9	2.9
6	1598.2	245.1	8.9
7	305.7	130.3	3.0
8	1622.6	247.2	10.2

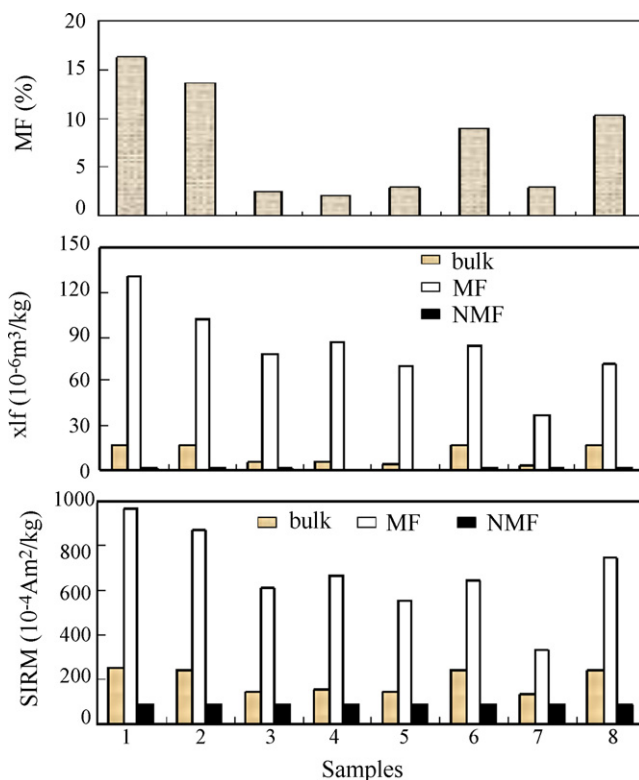


Fig. 2. Magnetic property values of magnetic fractions (MFs) and non-magnetic fractions (NMFs). (a) Amount of magnetic fractions, (b) Magnetic susceptibility (χ If), and (c) Saturation isothermal remanent magnetisation (SIRM).

left to settle for 5 min and filtered. Then, the filtrates were acidified to a pH of less than 1 with concentrated HNO₃. The total duration of the test was 160 ± 10 min and the temperature was maintained between 35 and 39 °C. All the leaching tests were carried out in duplicate. Concentrations of the heavy metal ions in the extracts were determined using an atomic absorption spectrophotometer (AAS).

3. Results and discussion

3.1. Mass and magnetic properties of MFs

The mass and magnetic values of MFs are shown in Table 1 and Fig. 2. The contents of MFs in fly ashes ranged between 2.2 and 16.3 wt%, and were found to be highly positively correlated with magnetic susceptibility (χ If) of the bulk fly ashes (MFs = 0.0082 χ If – 1.138, R^2 = 0.854, p < 0.01). Magnetic susceptibility values of the studied fly ashes are in a wide range from 305 × 10⁻⁸ to 1703 × 10⁻⁸ m³/kg. The magnetic susceptibility values of Chinese fly ashes are in the normal range as reported for other coal-burning power plants [8,9,34]. The typical magnetic susceptibility value for fly ashes was reported to be in a range from 500 × 10⁻⁸ to 3000 × 10⁻⁸ m³/kg [8,9,34]. The difference arises from several factors: initial Fe concentration in coals, different technological conditions during coal combustion, different solid-phase reactions, highest temperatures reached in power plant boilers, different initial mineralogy of coals and so forth. The magnetic susceptibility of MFs ranged from 3780 × 10⁻⁸ to 13,082 × 10⁻⁸ m³/kg (Fig. 2), which is about two orders of magnitude higher than those of the NMFs. Magnetic susceptibility of all NMFs is determined in a range from 40 × 10⁻⁸ to 56 × 10⁻⁸ m³/kg. The magnetic susceptibility values of the NMFs were in a range 2.8–13.9% of the bulk samples. The magnetic susceptibility of pure magnetite was

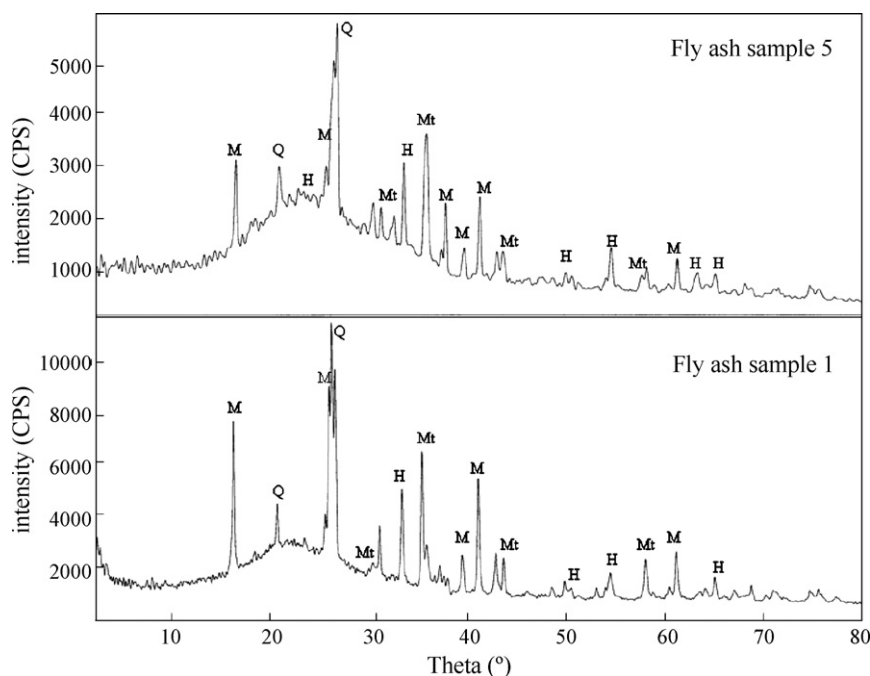


Fig. 3. X-ray diffraction (XRD) patterns of magnetic fractions of typical fly ashes. H—hematite, M—mullite, Mt—magnetite, and Q—quartz.

reported to be about 4.8×10^{-4} to $6.1 \times 10^{-4} \text{ m}^3/\text{kg}$ [31,34]. Based on the measured magnetic susceptibility of MFs and the reported value of magnetite, the proportion of magnetite-like phase was estimated as 0.1–0.33% pure Fe_3O_4 , indicating that the MFs do not consist of pure magnetic particles. Similarly, the non-magnetic fractions contain small amount of magnetic particles. Frequency-dependence of the magnetic susceptibility has been widely used for evidencing the presence of superparamagnetic ferrimagnetic grains (SP) [31,34]. The $\chi_{fd}\%$ of the studied ashes varied between 0% and 4.0%, which suggests the presence of relatively low amount of SP grains. This result is in a good agreement with the value of 1–4%, reported previously for the fly ashes of power plants and metallurgical industry [8,34].

The SIRM of the fly ashes is estimated in a range of $(130\text{--}254) \times 10^{-4} \text{ Am}^2/\text{kg}$. The SIRM values of MFs are 4–10 times greater than those of the NMFs. After removal of the MFs, the SIRM of the residue is decreased to $(84\text{--}92) \times 10^{-4} \text{ Am}^2/\text{kg}$. The SIRM values reflect contributions of all remanence-carrying minerals, including ferrimagnets and weakly magnetic minerals such as hematite and goethite. The SIRM values of NMFs suggest that they contain remanence-carrying minerals. Magnetic measurements showed that the fly ashes were characterized by the specific combination of high susceptibility value and low frequency-dependence magnetic susceptibility. Practically, all industrial fly ashes contain significant fraction of magnetic particles. Veneva et al. [8] reported that the strongly magnetic fraction constituted up to 10–15% of the total load in the power plant emissions, which results in magnetic enhancement of soils and sediments around emission sources. Thus, magnetic susceptibility of soils, sediments, and tree leaves around the emission sources of fly ashes can be used as an indicator of particulate pollution from fly ashes. Overall, fly ashes contribution to magnetic susceptibility of soils and sediments can vary due to proximity to industrial fly ash sources, redistribution by erosional processes and post-depositional dissolution. The magnetic susceptibility values can be used to estimate the pollution degree of fly ashes by establishing the magnetic susceptibility of unaffected soils and sediments as the background value. Therefore, magnetic analysis could be a powerful tool for environmental evaluation on

soils, sediments, and tree leaves affected by fly ashes emission. Although works on the determination of the distribution of magnetic spherules in air, water, and sediments have been reported [7,9–11], efforts are necessary to develop the magnetic selection criteria for the isolation of different pollution sources in soils and sediments.

3.2. Mineralogy of MFs

3.2.1. X-ray diffraction

Our previous work [35] has indicated that the mineralogical composition of the bulk fly ash is composed of mullite, quartz, calcite, and boehmite. Fig. 3 shows the XRD patterns of MFs extracted from fly ashes. All MFs samples have the similar X-ray diffraction patterns, indicating their similarity in the mineralogical composition. X-ray diffraction pattern verifies that both magnetite and hematite are main iron oxide phases in MFs. Other mineral phases include quartz and mullite. Diffraction intensities of these minerals are much higher in NMFs (data not shown). In all MFs samples, the peak intensity of magnetite is greater than that of hematite, indicating that crystalline iron in the magnetic fraction is present mainly as magnetite mixed with hematite, mullite and quartz in various proportions. As coal does not contain magnetite, the presence of magnetite in fly ashes must be a conversion from other iron minerals, such as pyrite (FeS_2), siderite ($\text{CaFe}(\text{CO}_3)_2$) and ankerite (FeCO_3), during coal combustion. Different boilers and combustion conditions resulted in different iron oxide phases, which are related to the combination of iron-bearing components and silicates in different temperatures and oxidizing or reducing conditions [21,36,37]. According to Ramsden and Shibaoka [38], magnetite was formed as a reduced part in the furnace and then was partially oxidized to hematite, which results in a mixture and close correlation of these minerals in fly ash. The main reason for the coexistence of magnetite, mullite, and quartz in MFs is that iron spherules were embedded in an amorphous aluminosilicate matrix and iron oxide crystallization in the aluminosilicate matrix. The magnetic extraction technique separated together these intimately associated minerals with magnetite [5,6].

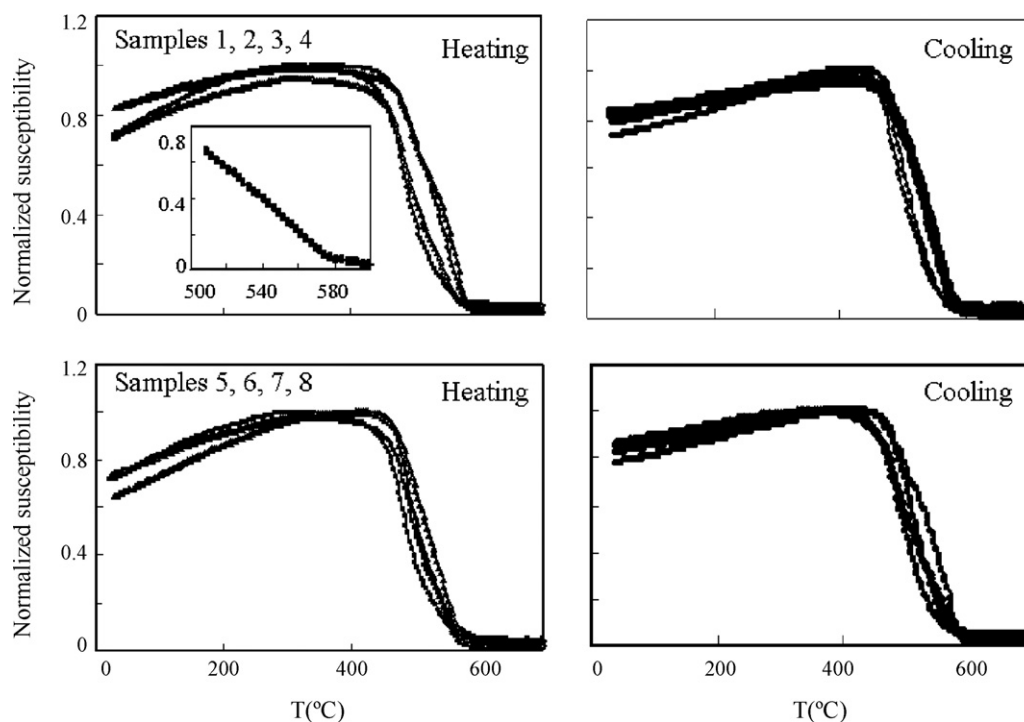


Fig. 4. Thermomagnetic analysis of high temperature variations of magnetic susceptibility for determination of Curie points of magnetic minerals.

3.2.2. Magnetic susceptibility versus temperature curve

The MFs were heated to 700 °C and then was cooled down to room temperature, during which the magnetic susceptibility was measured and plotted as a function of temperature in Fig. 4. In

spite of different sources, these samples showed very similar thermo-magnetic behaviors, which suggest the presence of magnetite with Curie point (T_c) of 560–580 °C. For all samples, their main decrease in magnetic susceptibility occurred in the temperatures between

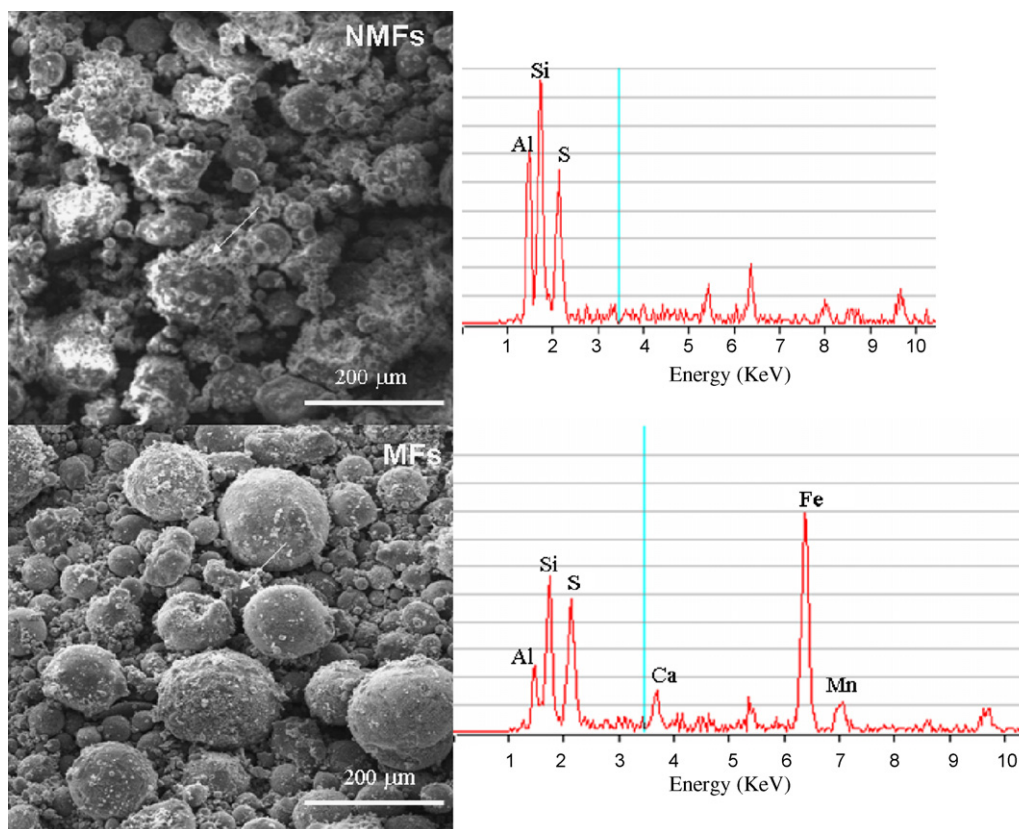


Fig. 5. SEM images and EDX spectra of typical magnetic and non-magnetic fractions. (a) Non-magnetic fraction particles, indicating irregularly shaped amorphous particles and sphere, (b) conglomerate of magnetic particles. Arrows indicate the points of EDX analysis.

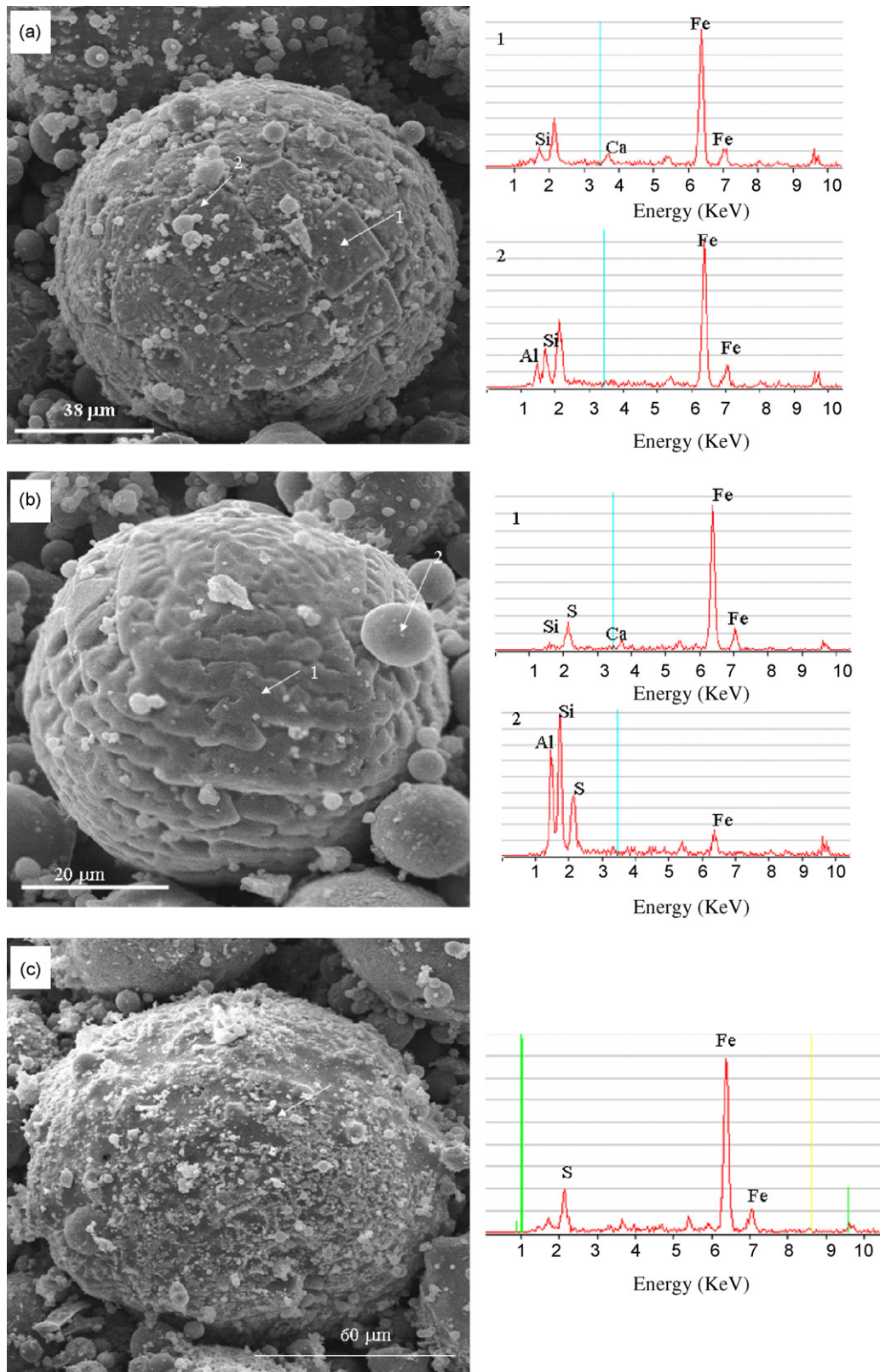


Fig. 6. SEM images and corresponding EDX spectra of the typical magnetic particles of fly ashes (arrows indicate the points of EDX analysis). (a) Iron spherule ($d=90\ \mu\text{m}$) with rough Fe oxide crystallization, (b) strongly magnetic dendritic Fe spherule ($d=60\ \mu\text{m}$) with adhered smooth alumino-silicate smaller particles on the surface where b-2 is the element composition of small spherule bound to magnetic particle, (c) granular Fe spherule ($d=120\ \mu\text{m}$). The external surface of the granular ferrosphere is rough, porous, and complicated by the additional presence of small granular crystals and molten drop.

450 °C and 580 °C. Various trace elements, such as Cr, Co, Ni, Cu, Zn, As and Pb, could incorporate in the magnetite structure, and replace Fe²⁺ and Fe³⁺ ions in the crystal lattice, which results in a decrease in the Curie temperature. As indicated in Fig. 4, the Curie points were near that of magnetite (580 °C), suggesting that substitution for Fe by different ions is low and does not cause a significant decrease in *T_c*. The weak decay in magnetic susceptibility above ~580 °C suggests the presence of hematite. Cooling from 700 °C to room temperature is often used as an indicator of the mineralogical/phase changes in the material during heating. All samples showed almost reversible thermomagnetic behavior. Reversible heating/cooling cycle and preservation of the same features on both curves suggest no mineral phase transformation occurring during heating. Analyses of magnetic mineralogy imply that the main magnetic minerals in MFs are magnetite, which is substituted with small amount of impure ions.

3.2.3. SEM/EDX

The SEM/EDX is capable of providing detailed imaging information about the morphology and surface texture of individual particles, as well as elemental composition of samples [39,40]. A general view of the magnetic and non-magnetic particles is shown in Fig. 5. Particle sizes of the fly ashes varied from less than 10 μm to greater than 150 μm, while those of the majority of magnetic particles ranged from 50 to 100 μm. The morphology and chemical data indicate that non-magnetic fractions are composed of over 80% amorphous aluminosilicate matrix and small amount of spheres. Particles in the non-magnetic fractions are much darker with a few bright particles. The particles with bright images contain significant amount of iron, which is probably due to the magnetic particles or hematite not removed during the extraction. Particles in MFs show much brightness and their shapes are mainly in spherical grain, irregular shaped amorphous grain and porous grain (Fig. 5). The main elements determined by EDX in the non-magnetic fraction samples are Si, Al, S, and small amount of K, Ca and Fe. The Ca and S in the EDX spectra for NMFs of fly ashes could be the presence of calcium sulfates or calcium ferrites. Similar results have also been demonstrated by Chen et al. [41] and Iordanidis et al. [39]. Spectra of the bright particles in MFs indicate higher iron content compared to those of the darker amorphous aluminosilicate materials. Although the relative amount of Al, Si and Fe in NMFs varied from particle to particle, the relatively weak signal intensity for iron indicates much lower concentration of iron in the particles. The data inferred from EDX spectra are consistent with the chemical analysis of the samples, as listed in Table 1.

Typical SEM images and EDX spectra of the spherical magnetic particles are shown in Fig. 6. These three images are indicative of typical iron spheres (ferrosphere) in MF samples. The iron spheres exhibit various morphology and textures on the surface of these particles (Fig. 6). Rough structure with coarse blocky surface crystallites was apparent in Fig. 6a, while a more dendritic pattern was found in Fig. 6b. SEM images in Fig. 6a and b also reveal particular surface morphology of the spherules (smaller grains attached to the surface of iron spheres), which is due to the high temperature processes in which the ashes are formed [36,40]. Major elements are determined on the surface of magnetic particles using EDX at one or two points. Total iron content ranged from 33.1 to 71.4 wt%. Qualitative elemental analysis shows that the main constituents except for Fe are Si, Al, S and Ca. EDX spectra of small smooth spheres indicate lower iron content compared to spectra of the larger sphere (Fig. 6b). The EDX results of the surface layers of magnetic particles show the presence of S element. This indicates that the surface of the magnetic particles is most probably coated with volatile compounds. Except for Cu, Mn and Zn, concentrations of the trace metals are too low to be determined by electron microprobe.

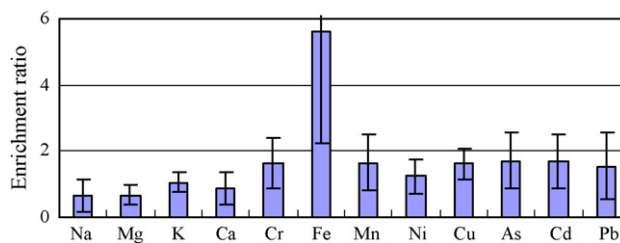


Fig. 7. Enrichment ratio of various elements in magnetic fractions, in which the enrichment ratio is defined as the ratio of element concentration in MFs and NMFs.

Fig. 6c exhibits irregular shaped spherical magnetic particles having high Fe content and rough surface. The granular crystals on the surface of the magnetic particles are a result of crystallization when temperature decreases. The concentration of iron in the magnetic particles is inversely related to that of Al and Si, which is expressed as high negative correlation coefficients of iron with other two elements ($R^2 = 0.899$ and 0.942 , respectively, $p < 0.01$). Correlation coefficients are calculated based on electron microprobe analysis of magnetic particles of MFs. The different morphologies and chemical compositions of the magnetic particles depend on the particular conditions, e.g. the viscosity of the melt, gases which are formed during burning of the organic materials, carbonates, sulfides, etc. [1,21,22,40].

In contrast to the magnetic particles of natural (pedogenic) origin, magnetic particles in MFs show specific morphology and distinct magnetic properties. The magnetic particles in fly ashes most often exist in a form of spherules, with relatively wide grain-size distribution, varying between several and hundred microns. The spherically shaped magnetic particles are commonly composed of pure or nonstoichiometric magnetite. Fe ions in magnetite or hematite phases are often substituted by other cations. Cr, Cu, Ni, Zn, As, and Pb are known to incorporate in the magnetite or hematite structure by replacing Fe²⁺ and Fe³⁺ ions in the crystal lattice. Thus, the presence of these magnetic particles in soils and sediments could be indicative of the atmospheric particulate pollutants by fly ashes.

3.3. Chemical composition of MFs

The range and average concentration of various metal elements in magnetic and non-magnetic fractions are listed in Table 2. Results in Table 2 show that the total iron contents in MFs and NMFs ranged in 23.4–66.4% (average 31.6%), and 3.0–22.6% (average 8.4%), respectively. As expected by mineralogy, Fe is depleted in NMFs and enriched in MFs. K and Ca have almost same enrichment in MFs and NMFs, while Na and Mg are nearly depleted in MFs. The enrichment ratios of elements, which are defined as the concentration ratio of elements in magnetic fraction and non-magnetic fraction, are illustrated in Fig. 7. The average enrichment ratio of Fe in MFs is calculated to be 5.6, which is much lower than that by Kukier et al. [6]. This can be attributed to the difference in the separation method of MFs. Kukier et al. [6] used a dry separation of magnetic rod, which is more effective in separating larger, strongly magnetic particles.

Fig. 7 also shows that the potential toxic metal elements Cr, Mn, Cu, As, Cd and Pb are enriched in the MFs. For example, Cr, which is likely associated with the magnetite, is much richer in MFs than in NMFs. Electron microprobe analyses show that Cr, Mn, and Cu are present in magnetic particles of MFs. Hulet et al. [19] used acid separation method and found that the concentrations of the first row transition metals in MFs were about ten-fold higher than those in NMFs. The fact that MFs contain significantly higher concentration of heavy metals as compared to NMFs suggests that Fe and other

Table 2

Chemical composition of MFs, NMFs and bulk fly ashes and enrichment ratio of elements in magnetic fractions (magnetic fractions/non-magnetic fractions).

Element	Element concentration (n=8)			Enrichment ratio
	Bulk fly ashes	Non-magnetic fractions	Magnetic fractions	
Na (%)	0.44–1.59 (0.92 ± 0.41)	0.59–2.82 (1.38 ± 0.94)	0.48–1.60 (0.88 ± 0.42)	0.68 ± 0.49
Mg (%)	0.40–1.81 (0.93 ± 0.51)	0.57–3.50 (1.58 ± 1.03)	0.37–1.73 (0.90 ± 0.49)	0.67 ± 0.29
K (%)	0.67–2.68 (1.76 ± 0.70)	1.04–2.17 (1.59 ± 0.38)	0.69–2.83 (1.79 ± 0.74)	1.06 ± 0.28
Ca (%)	2.34–20.11 (7.89 ± 6.68)	2.45–17.3 (7.89 ± 5.57)	2.32–20.8 (7.79 ± 6.91)	0.89 ± 0.49
Fe (%)	3.56–22.79 (10.38 ± 6.95)	2.97–22.59 (8.40 ± 7.45)	23.39–66.35 (31.55 ± 14.23)	5.60 ± 3.34
Cr (mg/kg)	10.89–32.02 (20.62 ± 7.10)	10.69–33.36 (20.55 ± 7.55)	12.93–58.3 (26.39 ± 14.94)	1.64 ± 0.77
Mn (mg/kg)	35.3–226.7 (136.2 ± 81.3)	34.4–200.1 (113.3 ± 70.8)	35.3–1204.0 (298.5 ± 397.5)	1.66 ± 0.84
Ni (mg/kg)	13.64–22.57 (18.93 ± 3.06)	13.73–22.65 (18.51 ± 3.39)	10.38–30.60 (22.10 ± 7.18)	1.23 ± 0.50
Cu (mg/kg)	8.86–24.90 (15.63 ± 5.75)	7.67–25.58 (15.15 ± 5.69)	8.95–47.33 (22.49 ± 14.82)	1.62 ± 0.46
As (mg/kg)	3.55–16.11 (8.14 ± 3.85)	3.02–17.59 (7.97 ± 4.58)	3.25–38.25 (12.51 ± 12.03)	1.71 ± 0.86
Cd (mg/kg)	0.42–2.56 (0.78 ± 0.73)	0.42–2.51 (0.67 ± 0.56)	0.39–6.37 (2.01 ± 2.53)	1.69 ± 0.83
Pb (mg/kg)	34.01–85.06 (62.66 ± 14.90)	33.66–83.50 (60.25 ± 14.08)	37.63–207.33 (90.51 ± 56.42)	1.54 ± 1.02

heavy metals such as Cd, Cr, Cu, Mn, and Pb (in particular Cr and Cd) are preferably gathered in magnetic fractions, as indicated by their significantly higher enrichment ratios. The enrichment mechanisms of these heavy metals (Co, Cr, Cu, Mn, Ni and Zn) on MFs are: (1) they are present in a form of isomorphous substitutions of the Fe oxide minerals by substituting Fe in the oxide crystal lattices; (2) these metals are adsorbed by iron oxides in MFs. The enrichment of heavy metals on MFs raises environmental concern issue with the fly ashes utilization and landfill. It suggests that removal of the magnetic fraction from fly ashes, especially as it comprised a considerable proportion of the bulk fly ash, would reduce significantly the amount of these heavy metals in fly ash residues and could diminish the pollution of heavy metals [3,5,6].

3.4. Potential leachability of heavy metals from MFs and NMFs

Because there is no relationship between the total metal concentration and its leachability in fly ashes, leaching tests are often used to determine the potential of a fly ash to contaminate ground water and threaten human health. The TCLP has been employed to determine whether a waste should be considered as hazardous waste and widely used to evaluate the environmental risk of polluted wastes [16,20,24]. The TCLP-extractable concentrations of Cu, Pb and Cr are presented in Fig. 8. The concentration of TCLP-extractable Cd for MFs and NMFs is below the detection limit of instrument (0.1 mg/L). The TCLP-extractable concentrations of Cr, Cu, and Pb for MFs are higher than those in NMFs. The concentration of TCLP-extractable Pb is considerably below the specific characteristic toxicity levels of 5.0 mg/L except for sample 1 where the concentration of Pb is 6 mg/L, exceeding the USEPA regulatory level of 5.0 mg/L [23].

The GJST test, a technique offering a simple and fast approach for the assessment of heavy metal bioavailability (especially Pb), was employed to measure the concentrations of various heavy metals in MFs and NMFs. The results (Fig. 9) indicate that concentrations of GJST-extractable Cd, Cr, Cu, and Pb in MFs are higher than those in NMFs, especially Pb whose concentrations in MFs ranged from 6.49 to 27.22 mg/L with an average of 16.20 mg/L, and ranged from 2.78 to 5.39 mg/L with a range of 4.17 mg/L for NMFs. A comparison of the results in Figs. 8 and 9 reveals that TCLP test gives lower dissolved metal concentrations than the GJST test, suggesting that the GJST test is more effective in extracting heavy metals. For example, the average concentration of Pb in MFs was measured to be 16.20 mg/L by GJST test and 2.29 mg/L by TCLP test, respectively. The Pb concentration in NMFs ranged from 0.36 to 2.75 mg/L and 2.78 to 5.39 mg/L with the TCLP and GJST, respectively. The mean ratio of GJST-extractable Pb/TCLP-extractable Pb is 6.7 and 3.6 for MFs and NMFs, respectively. Compared with GJST, the TCLP is relatively short-term leaching method for heavy metals. Note that the GJST is a relatively new technique, and so far there has been no defined

absolute threshold for leaching [31]. The difference in heavy metal leaching between the TCLP and GJST may result from the pH of the leaching solution during the test. Previous works on fly ashes leaching has shown that the most significant factor in elemental release is the pH resulting from the interaction of the leachant and the ashes [16,30]. The TCLP uses a relatively high pH (~5) and a low temperature and no chloride, while GJST is a strong acid solution and relatively high temperature. The GJST better simulates the chemistry of the stomach [31]. After the extraction, the pH in the TCLP

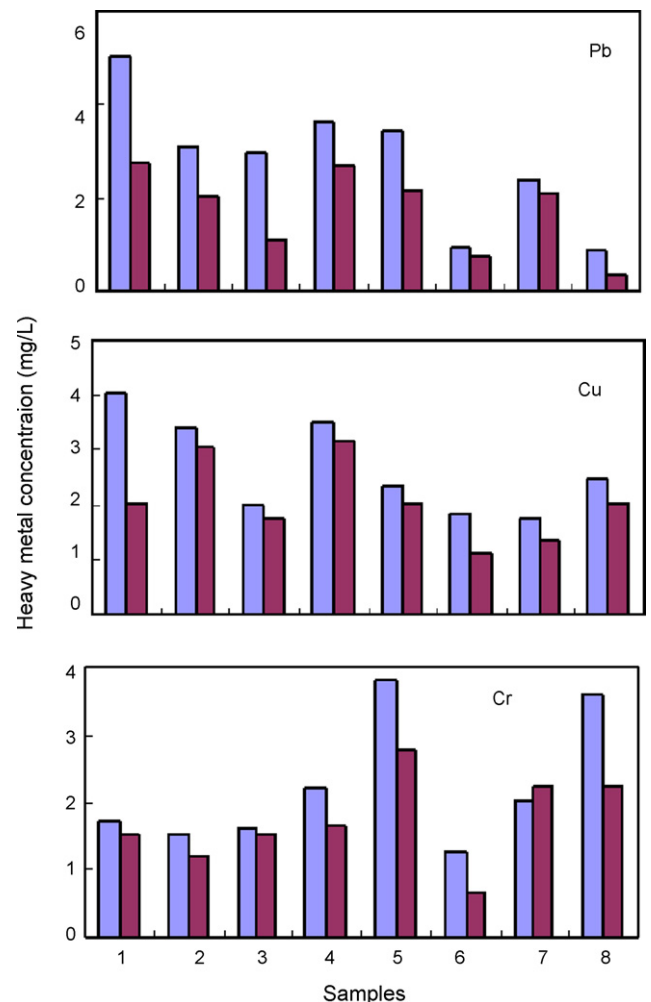


Fig. 8. TCLP-extractable Cr, Cu, and Pb concentrations in the magnetic and non-magnetic fractions. Note that the concentration of Cd was below the detection limit of the instrument.

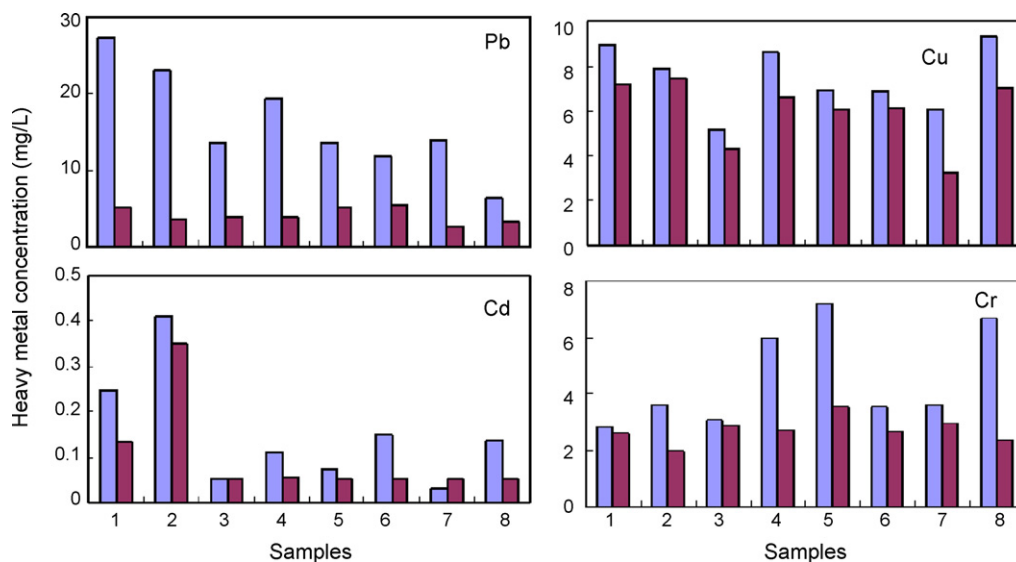


Fig. 9. GJST-extractable Pb, Cu, Cd and Cr concentrations in the magnetic and non-magnetic fractions of fly ashes.

extract was higher than in the GJST extraction. Low pH favor increasing the leaching rate of inorganic constituents due to an increase in the intensity of attack on the ash mineral phases that contain these elements.

A leachability ratio of heavy metal, defined as the ratio of TCLP and GJST-extractable heavy metal concentration divided by the total concentration, was calculated for each metal element and for each leaching method. Fig. 10 shows the leachability ratios of MFs and NMFs. Despite much higher heavy metal concentrations in the MFs, there was no substantial difference in the potential leachability of Cd, Cr, and Cu with TCLP and GJST tests between MFs and NMFs. The highest leachability ratio by TCLP for MFs was obtained for Cu (15.5%), followed by Cr (10.3%), and Pb (4.0%). The leachability ratio for MFs has the order of Cu > Cr > Pb > Cd. The leachability tests in Hellenic lignite fly ashes showed that Cd and Cr had a moderate mobility and As, Cu and Pb had a low mobility [42,43]. However,

leachability of Pb by GJST test in MFs was significantly higher than that in NMFs. The fraction of Pb leached from the MFs and NMFs under GJST was 22.3% and 7.5%, respectively. The high leachability shows higher potential hazard for the environment. Heavy metals in MFs exist in different forms, such as in an exchangeable form, an adsorbed form to the surface of iron oxide minerals, and a substituent form in the crystal lattice. The existing form of the heavy metals may have an important influence on the leachability. Metal ions held in the crystal lattice are not easily leached. Solubility of the surface-enriched elements is controlled mostly by dissolution, surface sorption, and complexation processes. Elements enriched in the cores of fly ash particles are not directly exposed to leaching solutions. Their release may be controlled by the dissolution rate of the surface layer of fly ash particles and by its related diffusion [6,19]. Further investigation on the potential mobility of heavy metals in MFs and NMFs is needed for better risk assessments.

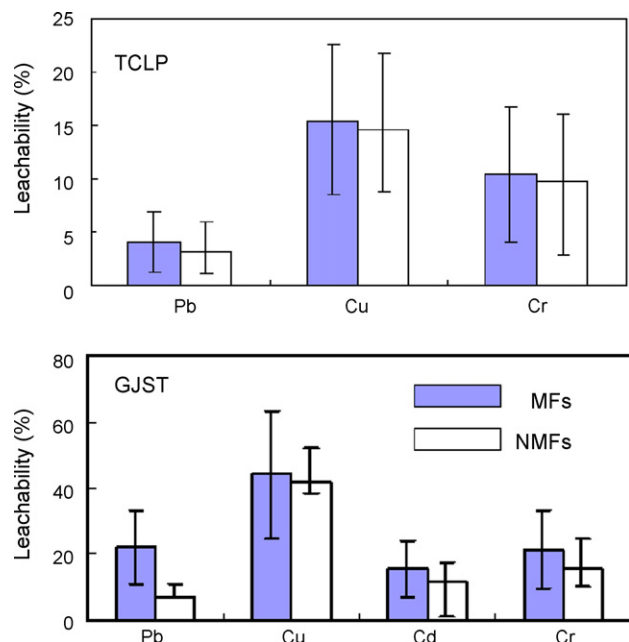


Fig. 10. Percentage of the TCLP- and GJST-extractable heavy metals over the total metal.

4. Conclusions

Magnetic fractions (MFs) of fly ashes from coal-burning power plants were extracted and analyzed using magnetic measurement technique. The MFs content of fly ashes ranged in 2.2–16.3 wt% (Fe, 23.4–66.4%) and was mainly composed of magnetic mineral phase magnetite. Other minerals such as mullite, hematite, and quartz also existed in MFs. It is estimated that magnetite content in MFs was in the range of 0.1–0.33%. The SEM images show that the magnetic particles existed in iron spherules with small difference in the surface texture and size. Typical iron spherules are characteristic of rough, dendritic and granular iron spherules. The EDX results show that the main elements in magnetic particles are Fe, Al, Si, S and small amount of trace element such as Cu, and Cr. The MFs was found to be enriched in Fe, Cr, Mn, Cd, Pb and Cu in comparison with the NMFs. The Fe gives the highest enrichment on MFs. The metal elements enriched in MFs occur dominantly as isomorphic substitution in the crystal lattices of Fe oxides and sorbed on surface of iron oxide. Due to higher concentrations of total heavy metals, the MFs has higher TCLP-extractable Pb, Cu, and Cr, and GJST-extractable Pb, Cd, Cr, and Cu concentrations. As for the metal concentration leached in MFs and NMFs by different extraction tests followed the order: GJST > TCLP. However, the percentage of heavy metals extracted by TCLP or GJST in MFs and NMFs has no significant difference, except TCLP-extractable Pb. The leachability ratios of potential toxic elements was in the order of Cu > Cr > Pb > Cd. The

metals have a great potential to be released into the environment under acid environment.

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