Mobility of heavy metals associated with the natural weathering of coal mine spoils

Zhi Dang[a,b,*], Congqiang Liu[b], Martin J. Haigh[c]

[a]*Department of Applied Chemistry, South China University of Technology, Wushan, Guangzhou 510641, People's Republic of China*
[b]*State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, People's Republic of China*
[c]*School of Social Sciences, Oxford Brookes University, Oxford OX3 0BP, UK*

"Capsule": *Natural weathering of coal mine spoils does not result in extensive release of heavy metals.*

Abstract

Knowledge of chemical mobility of heavy metals is fundamental to understanding their toxicity, bioavailability, and geochemical behavior. In this paper, two different methods, i.e. mineralogical means and sequential extractions, were employed to analyze the total contents, existing states, and chemical forms of heavy metals in coal mine spoils. The results demonstrate that the mobility of heavy metals in coal mine spoils depends not only on their existing states and the stability of their host minerals but also on the properties of the coal mine spoils. In the process of coal mine spoils–water interaction, sulfides that contain heavy metals first break down and release metals, which are then adsorbed and complexed by the iron oxyhydroxide colloid resulting from pyrite oxidization and organic matter. During the natural weathering of coal mine spoils, only a small fraction of these metals are released to the environment, and most of them still remains in the residual material © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The chemical forms of heavy metals in the solid phase can strongly influence their behavior, such as their mobility, toxicity, bioavailability, and chemical interactions, since metal speciation has deterministic control over physical, chemical, and biological processes that lead to transport and transformation of heavy metals among environmental compartments (air, water, biota, soil/sediment) in complex ecosystems (Allen et al., 1995). In the past three decades, much effort has been made to find a proper approach to assess the potential and actual impact of heavy metals in mining wastes. Approaches that have been used so far include determination of total concentration (Massey and Harnhisel, 1972; Aston and Thornton, 1977), laboratory simulation of tailings-water interaction (Cañibano et al., 1990; Jeng and Bergseth, 1992; Humez et al., 1997; Kedziorek et al., 1998), mineralogical forms of heavy metals (Fuge

et al., 1993; Walder and Chavez, 1995; Adamo et al., 1996; Davis et al., 1996), chemical extraction (Tessier et al., 1979; Soon and Bates, 1982; Cottenie and Verloo, 1984; Clevenger, 1990; Sauerbeck and Hein, 1991; Singh et al., 1996; Cooper and Morse, 1998; Ščančar et al., 2000; etc.), isotopic exchange (McLaren and Crawford, 1973; Frossard et al., 1994), and in-vitro acid extraction (Davis et al., 1993; Ruby et al., 1996).

Coal mine spoils are one kind of metal-rich industrial solid wastes (Massey and Harnhisel, 1972; Krothe et al., 1980; Szezepanska and Twardowska, 1987; Li, 1988; Cañibano et al., 1990; Jeng, 1992; Šebestová et al., 1996; etc.). Through coal mining, large quantities of this kind of wastes have been excavated from the underground to the surface of the earth. Natural weathering conditions may cause these exposed coal mine spoils to break down into small clay-size particles. Through this process, massive amounts of fine particles can then be released to the environment within the course of a few weeks (Taylor, 1974; Haigh, 1992). As metal sulfides, especially pyrite, are common components of all coal mine spoils, these metal sulfides can be oxidized easily during the natural weathering of coal mine spoils. Previous studies

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show that this process is controlled partly by micro-biological agents, notably, *Bacillus ferroxidans* (US EPA, 1971). If pH drops below 4, the hydrogen ions resulted from these agents can expedite the weathering of coal mine spoils and speed up the release of toxic elements (Pulford and Duncan, 1978; Colbourn, 1980; Costigan et al., 1981; Wiggering, 1993).

The aim of this work was to conduct a detailed risk assessment of heavy metals contamination around a coal mining area. Two different methods, i.e. sequential extraction and mineralogical analysis, were used to determine the chemical activity of heavy metals in coal mine spoils.

2. Experimental

2.1. Samples

Samples used for this study were collected from the surface coal mine sites at Blaenavon in south Wales, Great Britain (Fig. 1). Blaenavon is located on the northeastern outcrop of the South Wales coalfield in the uplands (380–430 m elevation) of northern Gwent. The local geology includes Quaternary deposits over-lying Carboniferous/Pennsylvanian strata that are mainly comprised of hard sandstone and very friable coal mine spoils as well as coal.

At Walters' Group Mine ('A' on Fig. 1) and Pwll Du Mine ('B' on Fig. 1), relatively fresh and totally

Fig. 1. Geological map of test sites. A, Walters' Group Mine; B, Pwll Du Mine.

weathered spoils were collected separately (Table 1). The physical distance between the two sites is no greater than 0.5 km, and the coal was excavated from the same geological seams. Both sites were subjected to land reclamation treatment, but in neither case were the treatments successful. Consequently, over large tract-surface areas, coal mine spoils are exposed at the soil surface. Because the weathering time for the coal mine spoil samples from the two sites are very different, samples collected from Walters' Group Mine are lumps while those from Pwll Du Mine are mainly powder-like.

2.2. Climatic background of the sample sites

The climate of the South Wales uplands is maritime and mild. Monthly mean air temperatures range from 2.5 °C in January to 15 °C in July. There might be about 100 freeze-thaw cycles each year, and the growing season lasts about 229 days from early April to November. The area receives an annual precipitation of around 1600 mm. In consideration of the mean annual temperature and the mean annual precipitation, the region belongs to a strong chemical weathering area (The Open University, 1990).

2.3. Total metal concentrations

Air-dried samples were oven-dried at 40 °C for 48 h, then crushed and sieved with a 150-mesh screen. After that, powders were placed in a clean porcelain crucible and heated in a muffle furnace at 800 °C for 5 h. About 0.5 g of the ashed sample was digested with 5 ml concentrated nitric acid, 10 ml hydrofluoric acid and 1 ml perchloric acid in Teflon beakers. Beakers with the fluid were first heated gently on a hot plate at a temperature of 80 °C for 3 h and then heated at a raised temperature of 170 °C until the samples were reduced to moist solids. The solid samples were allowed to cool to room temperature and rinsed with a few drops of deionized water. Samples were then leached in 5 ml concentrated HCl, the solutions were diluted with deionized water in 25 ml volumetric flasks, and analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES). By inserting duplicates (10%) into each batch of the samples, the precision of the data thus acquired can be controlled, and procedural blanks can be employed to check for contamination during analysis.

2.4. SEM and EPMA analyses

Electron probe for microanalysis (EPMA) and scanning electron microscopy (SEM) were used to determine the composition of the host minerals for heavy metals in coal mine spoils.

The major parameters of EPMA used in this experiment are: acceleration voltage, 25 kV; probe current,
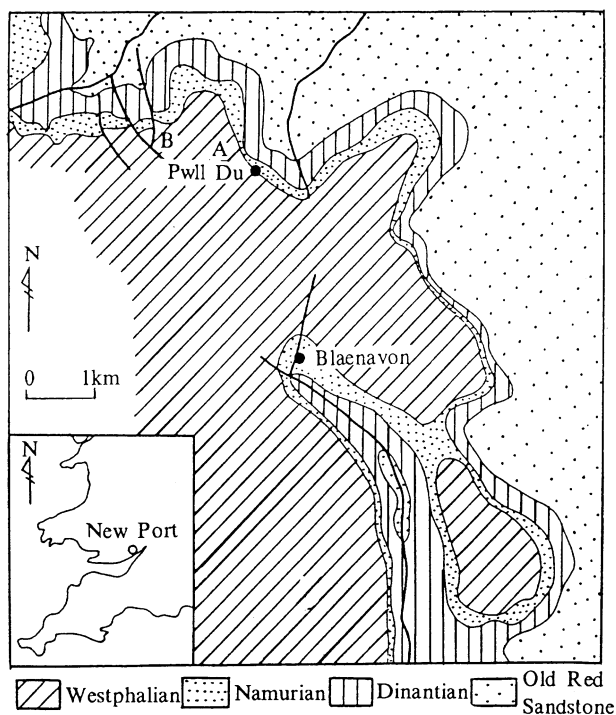
Table 1
Coal mine spoil samples collected from Blaenavon[a]

Sample no.	Position	Weathering degree	Exposing time to air (year)
W1	Top of spoil pile	Fresh, lump	<1
W2	5.5 m to bottom	Partly weathered, lump	∼3
W3	Bottom of spoil pile	Partly weathered, lump	∼3
P1	Top of spoil pile	Weathered, lump	∼50
P2	2.5 m to top	Weathered, lump	∼50
P3	5.0 m to top	Weathered, powder	∼50
P4	7.5 m to top	Weathered powder	∼50
P5	Bottom of spoil pile	Weathered, powder	∼50

[a] W, Walters' Group Mine: the distance from top to bottom is 11 m; P, Pwll Du Mine: the distance from top to bottom is ∼10 m.

2.5×10^{-8} A; electron beam, 2 µm. After being sliced up, polished and coated with carbon, coal mine spoil samples were then analyzed for the chemical composition of their mineral components.

Relevant instrumental conditions for SEM are: resolution of secondary electronic image, 60 Å; spatial resolution of back-scattered electronic image, 100 Å; and resolution of X-ray energy spectrum, 150 eV. The procedure for SEM examination and analysis of particles is as follows. Sample was first polished, mounted on a sample-stand, and coated with carbon. Mineral particles can then be examined in back-scattered electron mode. Finally, particles containing Cd, Cu, Pb, and Zn were analyzed semi-quantitatively using energy dispersive spectroscopy method.

2.5. Sequential extraction

Several different sequential extraction methods were used to evaluate the mobility of heavy metals for contaminated soils by a variety of scholars (Tessier et al., 1979; Mahan et al., 1987; Zhu and Alva, 1993; Bodog et al., 1997; Luo and Christie, 1998; and so on). Among these, Tessier's method (Tessier et al., 1979) was chosen for this research simply because it had been rigorously tested and was used as a model by many different investigators (Rauret and Rubio, 1989; Keller and Vedy, 1994; Urasa and Macha, 1996; Chwastowska and Skalmowaki, 1997; Tu, 1997).

After samples were analyzed for their total concentrations, ca. 1.0 g of each sample was weighed and put into a 50-ml centrifuge tube for the extraction experiment. Heavy metals in each sample were extracted using different agents following Tessier's method (Tessier et al., 1979). The analytical procedure involving sequential chemical extraction for the partitioning of particulate trace metals (Cu, Pb, Zn and Fe) can be divided into the following five steps:

Step 1 (exchangeable). The sample was extracted with 8 ml of 1M magnesium chloride at pH 7 under room temperature and agitated continuously for 1 h.

Step 2 (bound to carbonate). The residue from Step 1 was washed with 8 ml of distilled-deionized water and then extracted with 8 ml of 1M sodium acetate adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained for 5 h.

Step 3 (bound to Fe-Mn oxides). After washing with 8 ml of distilled-deionized water, the residue from Step 2 was leached with 20 ml of 0.04M hydroxylamine hydrochloride in 25% (V/V) acetic acid. This extraction was performed at 96 °C with intermittent agitation for 6 h.

Step 4 (bound to organic matter). Eight milliliters of 0.02M nitric acid and 5 ml of 30% hydrogen peroxide were added to the residue from Step 3, and then adjusted pH to 2 with nitric acid. Heat to 85 °C for 2 h and agitate occasionally. Add 3 ml of 30% hydrogen peroxide and again heat to 85 °C for 3 h with slow agitation. After cooling, added 5 ml of 3.2M ammonium acetate in 20% nitric acid, diluted the sample to 20 ml, and agitated continuously for 30 min.

Step 5 (residual). As lots of organic carbon compounds are left in the residue, extraction for Step 5 is omitted for this study. The concentrations of metals in the residue were obtained by subtracting exchangeable, bound to carbonate, bound to Fe-Mn oxides, and bound to organic matter from the total concentration.

During each step of the analytical procedure as stated above (excluding Step 5) and after the equilibrium was obtained, separation was achieved by centrifugation at 4800 *g* for 30 min. The supernatant was then removed by a pipette and placed in an acid-cleaned tube for concentration analysis, the residue left in the centrifuge tube was washed with 8 ml of distilled-deionized water and then extracted using a second reagent following Tessier's method. The extractants acquired during each step of the analytical procedure were finally analyzed for Zn, Pb, Fe, and Cu using ICP-AES.

3. Results and discussion

3.1. Total concentration of heavy metals

Recently published results, obtained from laboratory simulation of mine tailing-water interaction, demonstrate that the contents of heavy metals in tailings decrease with the reaction time (Geidel, 1979; Strŏmbergt and Banwart, 1994; Wang et al., 1994; Humez et al., 1997; Kedziorek et al., 1998; etc.). It can therefore be reasonably postulated that the concentrations of these elements in weathered samples should be lower than those in the fresh samples. When coal mine spoils are exposed to natural weathering conditions, the metals are first released and then migrate to surrounding water-soil-sediment, which resulted in contamination of ecological systems.
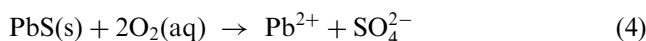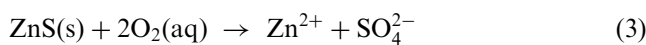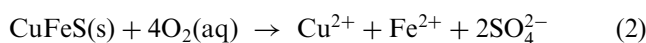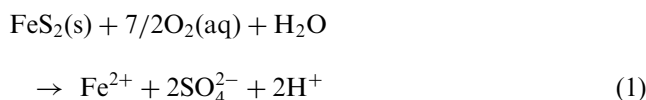
However, the analytical data in Table 2 exhibit an unexpected phenomenon: the contents of heavy metals in weathered samples are nearly equal to or even higher than those in relatively fresh samples. As there is no other source of heavy metals around heaps of coal mine spoils and their vicinity other than air input, the result implies that much of these metals still remain in the weathered samples and only a rather minor fraction of them is leached into the environment during the natural weathering of coal mine spoils.

3.2. Host minerals for heavy metals

When coal mine spoils react with water under natural weathering conditions, the stability of minerals that contain heavy metals is one of the major factors controlling the geochemical cycle of heavy metals. Study of the weathering sequence of Goldich (Goldich, 1938) indicates that the stability of minerals is related to their lattice energy. Heavy metals in host minerals having higher lattice energies would be more stable in spoils. During the weathering processes, such minerals would not be decomposed and would remain in the coal mine spoils. However, with the release of other components such as clay minerals, these metals could easily be enriched in the residual.

Results obtained by SEM and EPMA show that metals (Cu, Pb, and Zn) in samples exist mainly as independent sulfide minerals whereas Cd is hosted by other sulfide minerals that exhibit isomorphism (Table 3). In general, the chemical structures of these sulfides can be broken up easily through two different paths, dissolution or oxidation, during the weathering processes. As the aqueous solubility of these sulfides is very low, the dissolution is not usually regarded as a main way for the heavy metals to leave the coal mine spoils. Data in Table 4 reveal that the lattice energy values for these sulfides are nearly identical to that of calcite, and indicate that these sulfides would be unstable in a strongly chemical weathering area. Oxidation-reduction reactions would occur if these minerals are in contact with oxygen dissolved in water and be described as follows:

$$FeS_2(s) + 7/2 O_2(aq) + H_2O$$

$$\rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

$$CuFeS(s) + 4O_2(aq) \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-} \tag{2}$$

$$ZnS(s) + 2O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-} \tag{3}$$

$$PbS(s) + 2O_2(aq) \rightarrow Pb^{2+} + SO_4^{2-} \tag{4}$$

As the S^{2-} is oxidized into SO_4^{2-}, the crystal lattices of sulfides will break down immediately. So, heavy metals would be released from coal mine spoils and enter into the environment (Geidel, 1979; Backes et al., 1985; Cathles, 1994; etc.). This leaching process poses potential environmental and ecological effects on the weathering

Table 2
Content of heavy metals in ashed samples

Sample	Metal concentration ($\mu g/g$)			
	Zn	Pb	Fe	Cu
W1	38.86	82.89	22,730	21.04
W2	132.47	66.72	35,910	39.04
W3	45.97	70.10	13,389	17.03
P1	85.20	153.11	15,787	116.39
P2	77.73	10.42	14,772	136.30
P3	68.27	100.35	31,481	45.74
P4	62.69	105.24	27,343	63.81
P5	61.14	96.19	23,388	43.32

Table 3
Mineral composition of heavy metals in samples

Element	SEM unweathered	EPMA weathered
Cd	No independent mineral, co-existing with ZnS	No independent mineral, co-existing with ZnS
Cu	CuFeS$_2$	CuFeS$_2$
Pb	PbS	PbS
Zn	ZnS	ZnS

Table 4
The lattice energy of some minerals (kcal/mol)

SiO$_2$	CuFeS$_2$	FeS$_2$	PbS	ZnS	CaCO$_3$
1501	836	838	682.9	773.1	648

From Gao et al., 1984.

of coal mine spoils as has been described by most environmental scientists (Massey and Harnhisel, 1972; Krothe et al., 1980; Szezepanska and Twardowska, 1987; Querol et al., 1992; Wang et al., 1994; Šebestová et al., 1996; etc.). However, the data obtained from straight leaching could not be used to explain the concentrations of metals as indicated in Table 2.

3.3. Chemical speciations of heavy metals

The speciations of metals from sequential extraction could furnish detailed information about the origin, chemical forms, biological and physico-chemical availability, mobilization, and transport of trace metals. Each of the fractions extracted represents a different form and a different mechanism of availability. In the 'exchangeable fraction', the heavy metals are specifically adsorbed and are likely to be released when the ionic composition of water is changed. In the 'carbonate fraction' the metals are precipitated or co-precipitated and are susceptible to changes of pH. In the 'Fe-Mn oxides', the metals are adsorbed or co-precipitated and are unstable under reduction conditions. In the 'organic fraction', the metals are complexed and absorbed. Under oxidizing conditions, organic matter can be

degraded to result in the release of soluble metals. Metals in the 'residual fraction' are held in the crystal structures of some primary and secondary minerals. It is unreasonable to postulate that these metals can be released under the conditions normally encountered in nature. The distribution of heavy metals in different chemical species in coal mine spoils are presented in Fig. 2A–D.

As shown in Fig. 2, all of the heavy metals studied are predominantly in the residual fraction for coal mine spoil samples, no matter whether they are weathered or unweathered. This result might indicate that other components, e.g. clay minerals, carbonates, and so on, are released from samples during the weathering of coal mine spoils, and the heavy metals are still hosted in the residual fraction as they are very difficult to be leached out and tend to be gradually concentrated in the residual. It is consistent with the results of EMPA and SEM to a certain extent. Even for samples collected from Pwll Du, framboidal pyrite, frequently referred to as potentially the most reactive form of pyrite, can still be observed. It implies that the weathering rate of those sulfides may be affected by the matrix of coal mine spoil.

Compared with other chemical species in addition to the residual, the concentrations of metals that are in
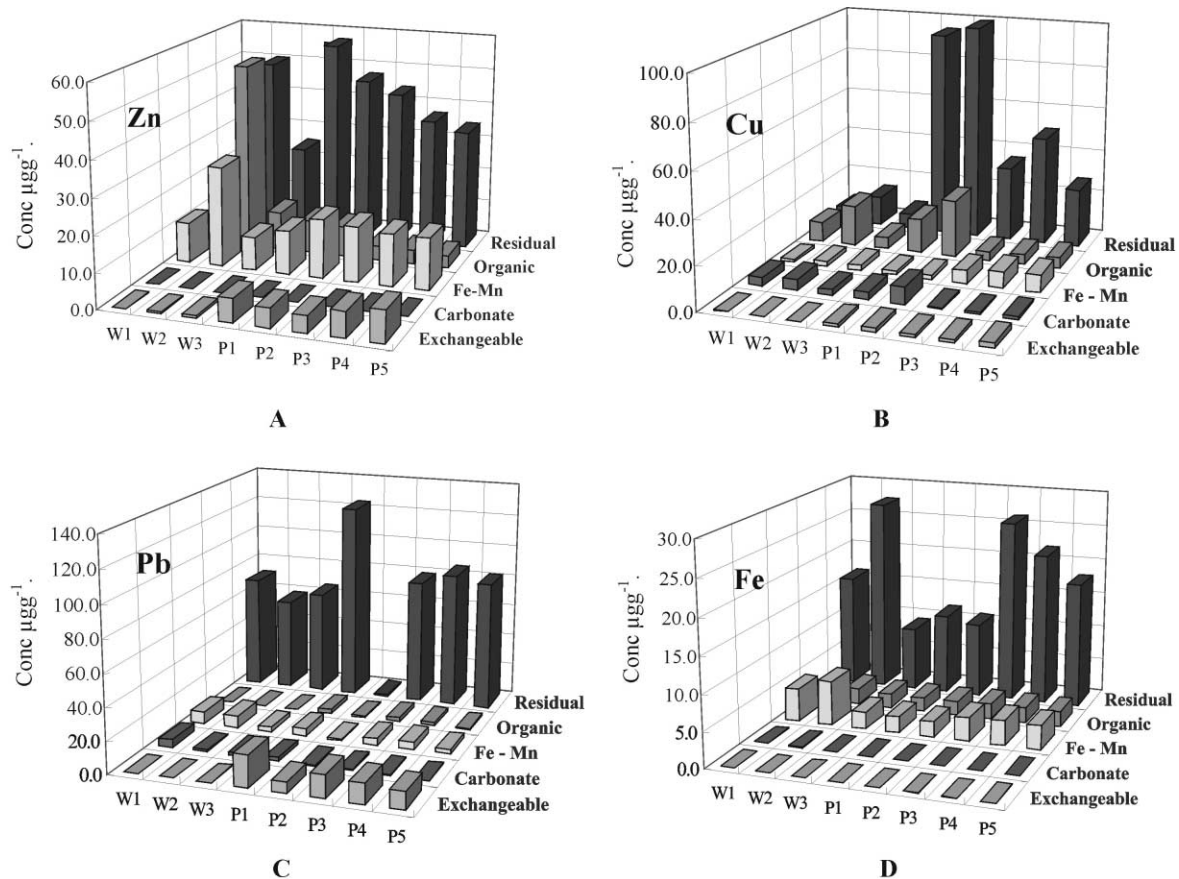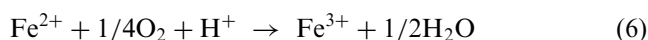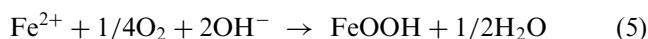

Fig. 2. Sequential extraction results for heavy metals. W1–W3 from Walters's Group Mine and P1–P5 from Pwll Du Mine.

bound to Fe-Mn oxides and organic matter are relatively higher than those of metals that are bound to carbonate and exchangeable. A possible explanation for the observed increase of concentrations of metals is that the metals from decomposition of sulfides are adsorbed or complexed by the iron oxyhydroxide colloid resulting from pyrite oxidization and by organic matter.

For ferrous ion, when it is oxidized by the dissolved oxygen in solution, the product is strongly dependent on the pH value. If the pH value is greater than 3.5, oxidation reaction follows Eq. (5) and form iron oxyhydroxide (Penkow and Morgan, 1981). On the contrary, when pH is less than 3.5, ferrous ion is oxidized into ferric ion as shown by Eq. (6) (White and Yee, 1985).

$$Fe^{2+} + 1/4O_2 + 2OH^- \rightarrow FeOOH + 1/2H_2O \qquad (5)$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad (6)$$

In this research, pH values of pore water collected from the pile of coal mine spoil were measured in the field. The results show the pH is near 5. Otherwise, the pH values obtained from experimental simulation of coal mine spoils–water interaction also indicate that the solution is weakly acid instead of strongly acid (Dang et al., 2001). These evidences support the concept that pyrite could be transformed into iron oxyhydroxide during the natural weathering of coal mine spoil.

Since iron oxyhydroxide colloid exhibits a strong affinity for heavy metals, it is very likely that part of the metals dissolved from sulfides could be adsorbed into this secondary phase (Johnson and Thornton, 1987; Carroll et al., 1998; Martinez and Mcbride, 1999).

In addition, ashing experiments demonstrate that about 80% of samples from weathered coal mine spoils can be turned into volatile matter and that only 20% remains as residue after ashing. However, samples from relatively fresh coal mine spoils can have 70% residual after ashing. It indicates that the residuum of samples from weathered coal mine spoils consists mainly of organic carbon compounds. As with iron oxyhydroxide colloid, this organic matter exhibit strong affinities for heavy metals (Tessier et al., 1996; Ghosh and Banerjee, 1997).

Another interesting phenomenon is that the proportion of the exchangeable fraction in weathered samples is obviously higher than that in relatively fresh samples. It implies that as the mobilization capability of these heavy metals in samples gets enhanced more metals would be transformed from other inert bounds into the exchangeable with time. Therefore, it can be inferred that the potential environmental impact of heavy metals on coal mine spoils is related not only to their total concentration and chemical forms, but also to the rate of weathering suffered by the samples.

4. Conclusions

Because hazardous wastes usually have complex compositions, the mobility of metals under natural weathering conditions is related to the properties of their matrix rather than to the total metal concentration and the stability of minerals containing the metals. To accurately predict the behavior of the heavy metals, a variety of approaches shall be employed all together.

Samples from the coal mine spoils for this study are mainly composed of silicates including clay minerals such as illite, kaolinite, and montmorillonite and quartz as well as some organic carbon compounds. In addition, small-sized sulfide minerals such as pyrite, chalcopyrite, and carbonate are also common. As coal mine spoils are exposed to natural weathering conditions, clay minerals can be released very quickly. It is consistent with results of previous research on these coal mine spoils which show that almost no clay and carbonate minerals exist in the Pwll Du samples (Dang et al., 1994). Metal sulfide minerals can also break down easily because they are vulnerable to oxidation when exposed to air and water. As has been demonstrated, the decomposition rate of these minerals is controlled by the bacteria in the environment (US EPA, 1971) and by the concentration of dissolved oxygen in water, consequently, these metals will be transferred from coal mine spoils in ionic states and into environment through diffusion. However, during the diffusion, they can be either complexed by the organic compounds or adsorbed by the amorphous iron oxyhydroxide colloid. The final result will be that much of the heavy metals still remain in the weathered coal mine spoils. Consequently, the pollution caused by the heavy metals from the coal mine spoils is limited. Nevertheless, points for attention should be made that the potential risk of pollution by heavy metals from coal mine spoils would increase with time since they can be converted from an inert state into an active state during weathering.

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