

## A Study on Chemical Speciations and Leaching Potential of Heavy Metals in Polluted Wastes Soils

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### ABSTRACT

Fractional compositions and leaching potentials of Cd, Cu and Zn were investigated in the soils which had been disposed with the metal processing wastes, tungsten mine tailings and low quality coal mine area. Total concentrations of metals in these soils were higher than in non-polluted paddy and upland soils. Fractions of Cd, Cu and Zn were mostly reducible, organic and residual forms, but varied with origins of wastes. Residual fraction was a predominant form in the non-polluted soils. Leaching potentials of metals were higher in polluted soils than in non-polluted soils. Metals leached were higher at pH 4.0 than 7.0 and increased with the duration time. After 25 to 35 hrs, metals released from soils reached a pseudoequilibrium. Leaching potential of metals in non-polluted soils was low due to high percentage of residual fractions.

**Key word** : Fractional composition, Leaching characteristics, Adsorbed, Reducible, Organic, Residual

### 요 약 문

석탄저장소, 텅스텐 광산의 광미, 고철 제련장내의 오염된 토양을 대상으로 중금속의 존재형태와 용출 가능성에 대하여 조사하였다. 석탄저장소와 광미, 제련장 지역 내 토양의 중금속 농도는 논과 비 오염지역의 산 토양보다는 높게 나타났으며, 대부분의 중금속의 존재형태는 reducible, organic과 residual fraction이 높게 나타났다. 오염되지 않은 토양의 중금속의 존재형태는 residual 형태가 주를 이루었다. 용출 가능성에 대한 평가는 오염되지 않은 토양보다는 오염된 토양에서 높게 나타났으며, pH 7.0 보다는 pH 4.0에서 시간이 증가함에 따라 용출량이 증가하였다. 오염된 토양으로부터 중금속의 용출은 Cu, Zn, Pb 등이 용출시간이 25시간 또는 35시간에 유사 평형에 도달했다. 오염되지 않은 토양의 낮은 용출은 중금속의 존재형태 중 높은 residual fraction의 비율에 의해 기인된 것으로 사료된다.

**주제어** : 존재형태, 용출특성, 흡착, 산화, 유기물, 잔존물

### 1. Introduction

Since the industrialization has been rapidly developed during past two decades, pollutants emitted from several industries have largely contributed to the environmental pollution in Korea.

These contaminants exceed the ability of natural purification mechanism of soil itself. Heavy metal pollutants from disposal of tailings, mining waste water, haulage, storage, sintering, refining, atmospheric discharges

and blowing dust.

Particularly, contaminants emitted from mining of the mineral resources and refining processes are transported in the vicinity areas, and then contaminate soils or stream water. In generally, fly ash or tailing produced from mining activity and refining processes contains large amount of heavy metals such as cadmium, copper, lead and zinc, etc (Alloway, B. J. and B. E. Davies, 1971). These metals are dispersed throughout the soils or surface water by the wind or rain. Metals in soil exist as the

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adsorbed on the surface or form organic complex within the soil layers by the interaction with organic matters in soils (Glenn, 1996).

Consequently, these contaminants have been discharged into the environment and may possibly have adversely influenced crop yields, animals and human health (Jung, 1995).

Until now, environmental problems have focused on the water pollution of stream or lakes used for the source of drinking water, but soil pollution has not merit the public concerns much because soils are prevalent and also often do not reveal the sign of contamination due to a high buffering capacity.

In general, contaminants in soil are stabilized by the natural purification of soils itself. Purification of contaminated soils is proceeded as a following two mechanisms; degradation of contaminants by soil microorganisms or adsorption on the soil surface (Tan, 1975).

Since the industrialization have been accelerated, many kinds of chemicals are used and various pollutants are emitted in the environment. These contaminants exceed the ability of natural purification capacity of soil itself. Particularly, it is well known that new chemicals recently produced inhibite the activity of soil microorganisms. Also, heavy metals adsorbed in soil are released by acid rain and enter into the stream or lakes, which can cause a secondary pollution problem.

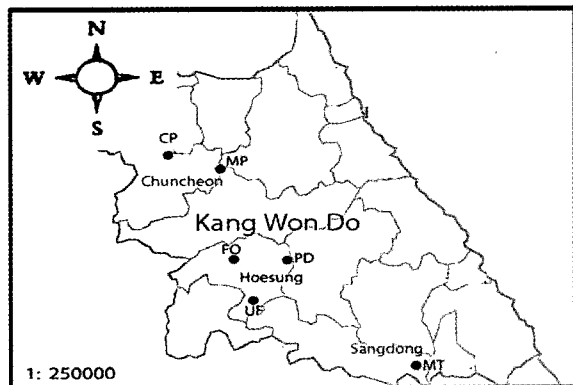


Fig. 1. Sampling location of soil samples in the KangwonDo.

It is necessary to compare the leaching characteristics of heavy metals in soil in to understand the reaction mechanisms soils and the degree of dispersion of contaminants emitted from pollution sources. In this research we investigate the fractional composition and leaching characteristics of heavy metals from soils both polluted and non-polluted with mining activities.

## 2. Material and Methods

### 2.1. Study Area

Samples are collected at two districts including Hoesung, Sangdong and Chunchon in Korea. The characteristics of samples are listed in Fig. 1 and Table 1.

In Table 1, paddy-field, upland field, and mountain soil are obtained at Hoesung district located in Korea. This area is kept apart from the industrial activities which may be contaminated. Bongsan soil is sampled in Hoesung industrial park which several industries have been operated since 1970s. Therefore, this area is completely exposed to the pollutant emitted from the industrial processes. Coal storage soils is collected at the area that have been used as a coal storage basin until the recent. Tailing is collected in Sangdong mine which has been produced zinc mineral between 1916 and 1992.

### 2.2 Experimental Section

#### 2.2.1. Sampling

Soil and tailing samples are collected on July 14, 2002. Soil samples are collected from a depth of 10~15 cm at the districts of Hoesung and Chunchon in Korea. Tailing from Sangdong mine is obtained from a pile of tailing. To obtain representative soil sample, sampling location is subdivided into smaller areas, 20 in number, and one sample unit is taken along a zig-zag path through the field.

#### 2.2.2. Pretreatment of samples

Soil samples are passed through an aluminum sieve with a 2 mm mesh. Materials including rock, organic matter not passing through the sieve are discarded. The < 2 mm soil samples are mixed manually to homogenize and then allowed air dry. The dried samples are stored in

Table 1. Descriptions of soil samples

Sample i.d.	soil sampling locations	site characteristics
PD	Paddy soil	Reference soil, no pollution source found
UF	Upland Field soil	Reference soil, no pollution source found
FO	Forest soil	Reference soil, no pollution source found
MP	Metal Processing Plant soil	contaminated by metal processing wastes
MT	Mine Tailing Dam tailing	contaminated by tailing from wolfram mine
CP	Low Quality Coal Pile	contaminated by coal fly ash

polyethylene bag until analysis. Size distribution, organic nitrogen, and ignition loss of soil sample are carried out the range of soil diameter < 2 mm. And soils less than 64  $\mu\text{m}$  are used to the fractional composition and leaching tests of heavy metals.

### 2.2.3. Chemical analysis

Ignition loss of soils samples is determined by measuring the weight of samples before and after heating at 550°C for 2 hours. Content of organic nitrogen is determined by Kjeldahl method (APHA, 1989). Size distribution of soils is measured by sieve and pipette method (Park, 1983) and the classification of soil structure is determined by Shepard method (Shepard, 1954). Humic levels of soil is determined as the ratio of organic nitrogen to ignition loss and classified into three stages as following. the values of < 20, oligohumic; the values between 20 and 25, mesohumic; over 25, polyhumic (Hakanson, 1983).

### 2.3. Sequential Extraction Procedures (SEPs)

Sequential extraction is performed on a subsample using a method described by Tessier et al. (1979). According to this method, the fractional composition of heavy metals may be classified into five fractions as follow: adsorbed, carbonate, reducible, organic, and residual fraction. Sequential extraction procedures are illustrated in Table 2 and the properties of each fraction are as following.

Adsorbed metals exist on the surface of soils as an adsorbed form, which are labile under the changes of pH and cation concentrations in water solution. Carbonate metals are related with carbonate. These metals may be released under the acidic environment. Metals bound to iron and manganese oxides are referred to as “reducible metals”, which may be leached under the reducible environment. Organic metals are associated with various forms of organic matter or sulfur minerals. These metals may be released when organic matter degraded under oxidizing conditions. Residual metals are related with primary or secondary minerals which may hold the metals within their crystal structure. Therefore, these metals may not be leached in natural environment.

### 2.4. Leaching characteristics

To investigate the leaching characteristics of heavy metals in tailing and soils, experimental conditions are provided in Table 2. As shown in Table 2, a 1 : 10 solid/liquid ratio (w.w) is employed for the leaching tests. Fifty grams portions are added to 500 mL deionized water and shake on a water bath shaker at 25°C for the desired contact time. Two kinds of leaching solution are used to determine the behavior of heavy metals according to pH (pH 4, pH 7). The initial pH of leaching solution is adjusted with 1N HCl. After shaking, the leachate is filtered using the glass fiber filters of 0.45  $\mu\text{m}$  pore size.

**Table 2.** Sequential extraction procedure(Tessier et al., 1979)

Chemical fraction	Extraction technique	Procedure
① Exchangeable metal	Exchange with excess cations	8 mL 1M-MgCl <sub>2</sub> (pH 7.0), shaking for 5 h at room temperature.
② Carbonate metal	Release by mild acid	8 mL 1M-NaOAc (pH 5.0), shaking for 5 h at room temperature.
③ Reducible metal	Reduction	20 mL 0.04M-NH <sub>2</sub> OH · HCl, shaking for 6 h at 96 ± 3°C.
④ Organic metal	Oxidation	3 mL 0.02M-HNO <sub>3</sub> + 5 30% H <sub>2</sub> O <sub>2</sub> (pH 2.0), shaking for 2h at 85 ± 2°C. 3 mL 30% H <sub>2</sub> O <sub>2</sub> , shaking for 3 h at 85 ± 2°C. After cooling to room temperature, 5 mL 3.2M-NH <sub>4</sub> OAc (in 20% HNO <sub>3</sub> ), shaking for 0.5 h.
⑤ Residual metal	None	2 mL HClO <sub>4</sub> + 10 mL HF, digestion to near dryness. 1 mL HClO <sub>4</sub> + 10 mL HF, evaporation to near dryness. 1 mL HClO <sub>4</sub> evaporation until the appearance of white fumes.

### 3. Results and Discussions

Table 3 shows the physical and chemical properties of samples. The pH of samples varies from 5.4 to 8.9. The lowest pH is observed in paddy-field soil and pH of tailing from MT is the highest in all samples. These results suggest that the acidification of soil is not serious in most of soils except PD soil.

Compared to field soil, PD soil, however, is highly acidified due to the agricultural activity.

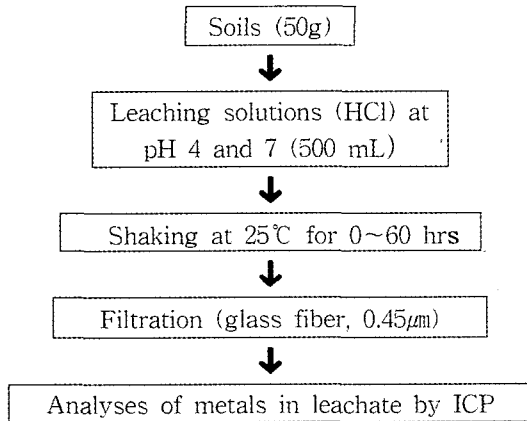


Fig. 2. Descriptions of Leaching Potential.

Table 3. Physical and chemical properties of samples

Sample type	soil texture	Ignition Loss(%)	Humic level	pH
PD	Siltysand	3.1	polyhumic	5.4
UF	Siltysand	5.0	polyhumic	6.8
FO	Siltysand	9.5	polyhumic	—
MP	sand	8.6	polyhumic	8.3
MT	Siltysand	0.1	oligohumic	8.9
CP	sand	6.5	polyhumic	7.9

— : not measured

In previous study (Jun, 1990) most of soils sampled from the Yeochon industrial park appear to be acidified as the pH of soils is 4.9~5.3. The status of humic substances in soils of most sites are polyhumic which organic matter is completely degraded, but tailing from MT is oligohumic, suggesting that the organic matter in tailing is degrading now<sup>10</sup>. From the size distribution of samples, it shows that MP and CP soil are sandy soil and the other samples are silt-sand soil.

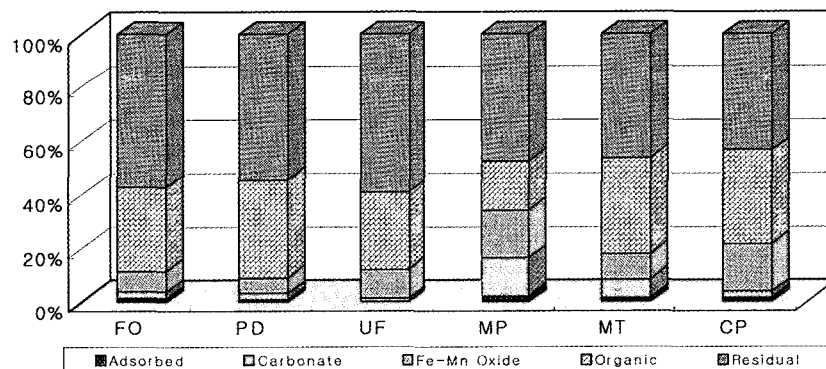
#### 3.1. Fractional Composition

##### 3.1.1. Cd

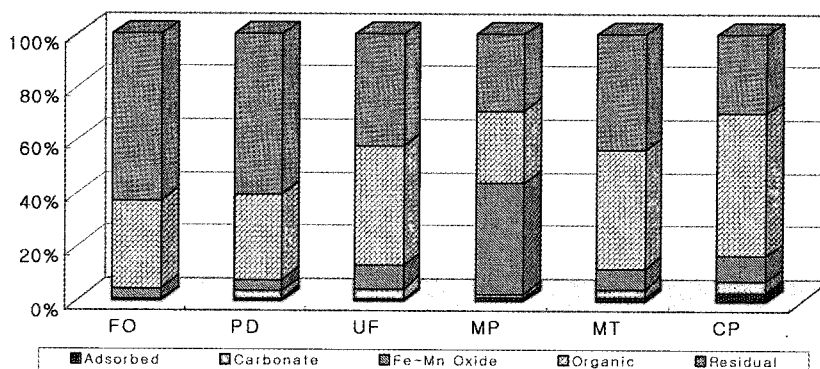
Fractional composition of cadmium in samples is listed in Fig. 3. The adsorbed fraction of Cd in PD, UF, and FO soils are not detected. 1.2% of Cd in MP soil, however, exist in the form of adsorbed fraction. And less than 1% of Cd in tailing is adsorbed fraction which is easily leached under the change of pH and cation concentration. 1.1% of Cd in coal storage soil exist as the adsorbed fraction, which is similar to MP soil.

Carbonate fraction of Cd is 1.1% of total content in PD soil and UF soil. But carbonate fraction of Cd in mountain soil is not observed. For the contaminated soil and tailing, carbonate fraction of Cd is 2.4% in MP soil, 2.5% in tailing from Sangdong mine, and 2.2% in CP, respectively. It is about 2 orders higher than those of noncontaminated soils. As the heavy metals of carbonate fraction may be probably leached under the slightly acidic environment, it is expected that leachability of Cd in contaminated samples is larger than those of noncontaminated soils.

About 11% of Cd is bound to iron or manganese oxides in PD and UF soil. Reducible fraction of Cd in mountain soil is 23.5% of total content, which is the largest in all samples. As the reducible fraction of Cd in MP soil and MT soil is between 2.4% and 5.9%, which is relatively low compared to the other samples.



PD; Paddy soil, UF; Upland Field, FO; Forest soil, MP; Metal Processing Plant soil, MT; Mine Tailing, CP; Low Quality Coal Pile  
Fig. 3. Fractional composition of cadmium in soil.



PD; Paddy soil, UF; Upland Field, FO; Forest soil, MP; Metal Processing Plant soil, MT; Mine Tailing, CP; Low Quality Coal Pile  
**Fig. 4.** Fractional composition of copper in soil.

The organic fraction of Cd is the largest in tailing from MT soil and decrease in order of UF, PD, CP, MP and FO soil. Considering that humic levels of MT soil is oligohumic, it is expected that large amount of Cd in MT soil may be released under the strong oxidizing condition.

Residual fraction of Cd is relatively high in soils of most sites, suggesting that large amount of Cd is stable in natural environment. The residual fraction of Cd in MT soil, however, is 35.6% of total content, which is relatively low compared with others. Other workers (Jun, 1990) find that the largest amount of Cd exist as the residual fraction.

As mentioned above, it seems that small amount of Cd in soils sampled at district of PD, UF, FO may be released within a short-term due to the low percentage of adsorbed and carbonate fraction, respectively. Over 60% of Cd in MT soil, however, is associated with Fe/Mn oxides or organic matter, indicating that large amount of Cd under the reducible or oxidizing conditions is probably released. The amount of adsorbed and carbonate fraction in samples contaminated, however is higher than that of noncontaminated soils, indicating that source of Cd is derived from the industrial activities.

Total concentration of Cd in the ranges of 0.0~23.6  $\text{mgkg}^{-1}$ . Highest concentration (23.6  $\text{mgkg}^{-1}$ ) was observed in the Metal Processing Plant soil (MP), but lowest concentration (0.0  $\text{mgkg}^{-1}$ ) was shown at the forest soil (FO). Metal Processing Plant soil concentration exceeded the corrective action level of 4.0  $\text{mgkg}^{-1}$  as designated in the Soil Environment Conservation Law (Ministry of Environment, 1999). Also, these concentrations exceeded the levels of natural abundance reported by several researchers (0.11~3.0  $\text{mgkg}^{-1}$ , by Pais and Jones, Jr., 1997). Result indicated that soil samples contaminated with cadmium.

### 3.1.2 Cu

The fractional composition of copper is provided in

Fig. 4. The adsorbed fraction of Cu is 5.5% of total content in PD and 9.0% in UF soil, but not detected in mountain soil. And the adsorbed fraction of Cu in samples contaminated by industrial activity is 0.5% of total content in MP soil, 0.2% in tailing from Sangdong mine (MT), and 0.9% in CP soil, which is less than that of soils not affected by industrial activity, respectively.

Carbonate fraction of Cu is 11.0% in PD soil and 8.2% in UF soil. It is not detected in FO soil. For the contaminated samples, carbonate fraction of Cu is 0.3% in MP soil, 2.4% in MT soil, and 1.4% in CP soil.

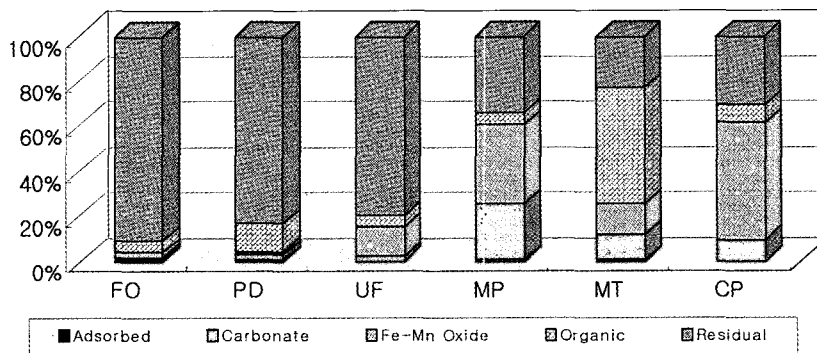
Reducible fraction of Cu in soils sampled at PD, UF, FO soil district ranges from 2.4% to 18.9% of total content. It is 49.3% in MP soil, 6.4% in tailing (MT), and 16.7% in CP soil. Particularly, as reducible fraction of Cu in MP soil is 2.5~20 orders higher than that of other samples, it seems that high levels of Cu may be leached under the reducible environment.

Organic fraction of Cu is relatively high in all samples except the MP soil. Organic fraction of Cu is 69.1% of total content in tailing (MT) from Sangdong mine. Considering that the status of humic substances in tailing is oligohumic, it is expected that large amount of Cu in tailing may be leached in a long-term. And residual fraction of Cu is the largest in FO soil, which is 84.3% of total content. Residual fraction of Cu in MP soil and MT soil is relatively lower than that of other samples, suggesting that large amount of Cu may be leached in these samples.

From the above results, large amount of adsorbed and carbonate fraction in PD and UF soil is observed, but not found in FO soil. The fractional composition of Cu is a striking contrast with Cd. It suggests that the agricultural activities is important in soil contamination by Cu.

### 3.1.3. Zn

The fractional composition of zinc in samples is provided in Fig. 5. The largest amount of Zn in PD soil is associated



PD; Paddy soil, UF; Upland Field, FO; Forest soil, MP; Metal Processing Plant soil, MT; Mine Tailing, CP; Low Quality Coal Pile  
**Fig. 5.** Fractional composition of zinc in soil.

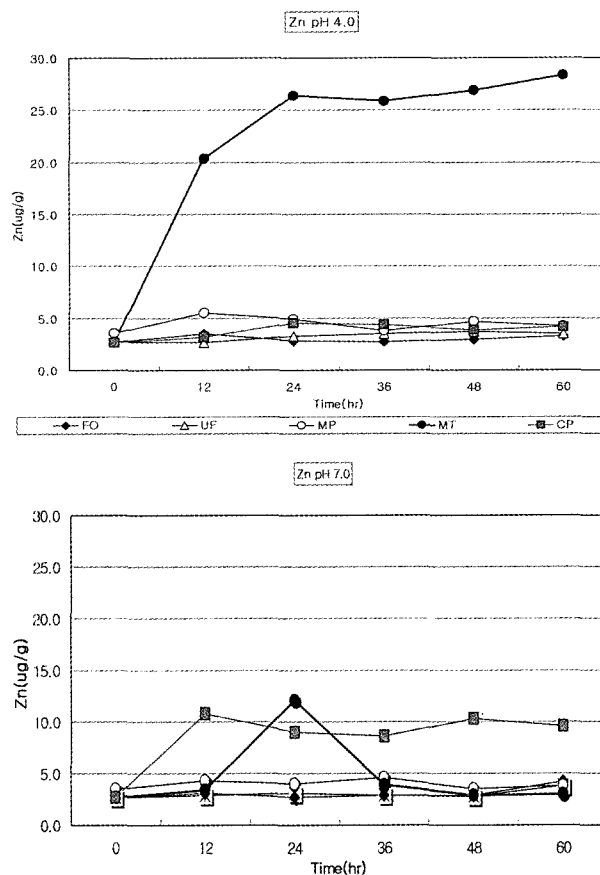
with residual fraction which is stable in natural environment. Organic fraction of Zn in PD soil is 7.4% of total content. Adsorbed, carbonate, and reducible fraction of zinc in PD soil are not detected.

81.5% of Zn in UF soil is related with primary or secondary minerals. 13.4% of Zn is bound to iron or manganese oxides, which may be released under the reducible conditions. Organic fraction of Zn in UF soil is 5.1% of total content, but the adsorbed and carbonate fraction of Zn in UF soil are not observed.

For FO soil, residual fraction of Zn is 94.3% of total content, which is the largest in all samples. And 5.7% of Zn in FO soil is related with organic matter. There is no existence in the form of adsorbed, carbonate, and reducible fraction.

Less than 1% of Zn in MP soil exist as the adsorbed fraction which may be released by the change of pH and cation concentration. 25.2% of Zn is associated with carbonate, which is 10 orders higher than that of Cd and Cu. Reducible fraction of Zn in MP soil is 35.2% of total content, which may be leached under the reducible condition. Organic fraction of Zn in MP soil is 5.2% of total content, which is similar to field and mountain soil. Residual fraction of Zn is 34.0% comparable with the reducible fraction, respectively.

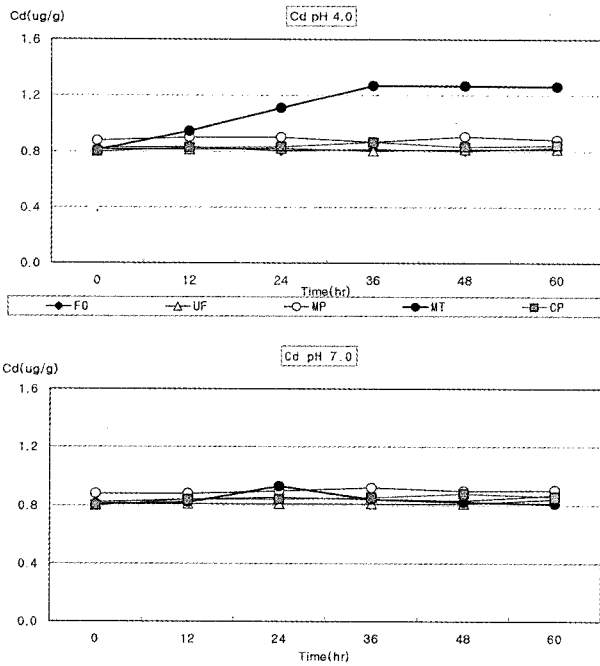
Similar to the Cd and Cu, fractional composition of Zn in samples is differently observed according to pollution sources. Particularly, percent levels of Zn in MP soil, MT soil, and CP soil contaminated by industrial activities exist as the adsorbed and carbonate fraction which may be leached in short-term. Large amount of Zn in PD, UF and FO soil, however, is associated with primary or secondary minerals, which indicating that probability of Zn to be leached is very low in natural environment. In case of contaminated samples, high percent of adsorbed and carbonate fraction and low percent of residual fraction are observed. These results indicate the probability of Zn pollution by acting the industrial activity.



PD; Paddy soil, UF; Upland Field, FO; Forest soil, MP; Metal Processing Plant soil, MT; Mine Tailing, CP; Low Quality Coal Pile  
**Fig. 6.** Release of zinc from soil sample at pH 4.0 and 7.0.

**3.2. Leaching Characteristics**

Fig. 6, 7, 8 shows the results of leaching tests performed from samples at pH 4.0 and 7.0. The amount of Cd leached is constant regardless of leaching time except tailing from MT soil. Concentration of Cd leached in tailing (MT) from Sangdong mine increases up to until 36 hours, and then maintain constantly. 1.5 µg/g of Cu in MP



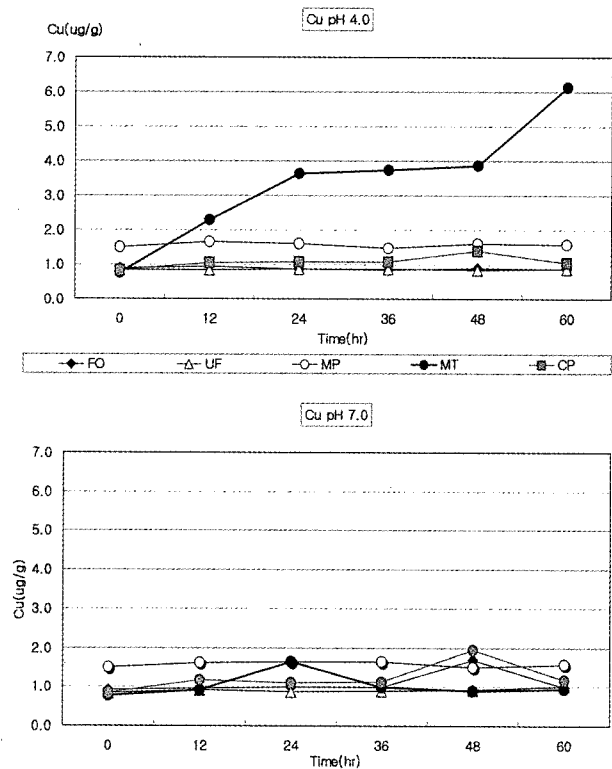
PD; Paddy soil, UF; Upland Field, FO; Forest soil, MP; Metal Processing Plant soil, MT; Mine Tailing, CP; Low Quality Coal Pile

Fig. 7. Release of Cd from soil sample at pH 4.0 and 7.0.

soil is initially leached, which is the highest concentration in all samples. As a leaching time elapsed, concentration of Cu leached appear to be nearly constant. 0.8 µg/g of Cu in tailing (MT) from Sangdong mine, however, is leached at the initial time and then increase to 60 hours. After 60 hours, the amount of Cu leached is 7 orders higher than that of the initial values. The amount of Zn in all samples appear to be constant regardless of leaching time except tailing (MT) from Sangdong mine. Concentration of Zn leached in tailing appear to be rapidly increased to 24 hours and then constantly maintained. However, comparing to the initial values, the amount of Zn leached in MT soil is about 10 orders higher at 60 hours. As higher levels of Zn in tailing is associated with organic matter, it seems that the amount of Zn leached may be increased with the increase of leaching time.

The results of leaching tests performed at pH 7.0 shows in Fig. 7. The amount of Cd leached is 0.9 µg/g in PD, MP, and CP soil after 60 hours. It is found that the leached amount of Cd is indepent on leaching time. For MP soil, concentration of Cd leached at pH 7.0 is as much as at pH 4.0. The amount of Cd leached in MT soil is 0.8 µg/g, which is less than that of pH 4.0. Comparing to pH 4.0, is shows that concentration of Cd in most of sites is relatively high except tailing.

The concentration of Cu leached varies from 0.9 µg/g to



PD; Paddy soil, UF; Upland Field, FO; Forest soil, MP; Metal Processing Plant soil, MT; Mine Tailing, CP; Low Quality Coal Pile

Fig. 8. Release of copper from soil sample at pH 4.0, 7.0.

1.6 µg/g. It is 1.0 µg/g in PD soil and UF soil, 1.6 µg/g in MP soil, 0.9 µg/g in MT soil, and 1.2 µg/g in CP soil, respectively. Also, it is observed that the amount of Cu leached is nearly constant regardless of leaching time. For MT soil, however, concentration of Cu appears to be increased to 24 hours and then decreased. Comparing to pH 4.0, the amount of Cu slightly increase in PD, UF, and CP soil, which is similar to the behavior of Cd. In case of MT soil, however, the leached amount of Cu at pH 4.0 is 5 orders less than that of pH 4.0 and independent on leaching time. As the organic fraction of Cu in tailing is about 70% of total content, it seems that large amount of Cu associated with organic matter is to be released under the strongly acidic condition of pH 4.0.

The amount of Zn leached varies from 3.0 µg/g to 9.6 µg/g, and depends on leaching time, respectively. Concentration of Zn leached in PD soil and UF soil is nearly constant to 48 hours and then dramatically increase. On the other hand, concentration of Zn in MP soil increases to 36 hours and then decreases until 60 hours. For MT soil, the largest amount of Zn is 12.1 µg/g at 24 hours of leaching time, which is 4 times of the initial values. After 24 hours, concentration of Zn in MT soil is

observed to be decreased. Compared to pH 7.0, the final values of Zn leached is 3.0  $\mu\text{g/g}$ , which is 9 orders less than that of pH 4.0. The amount of Zn in CP soil is the largest after 12 hours elapsed, and then constantly maintained. Concentration of Zn is largely dependent on leaching time, which is different to the behavior of Cu and Cd.

Comparing this results with the previous results (Hakanson, 1983), the amount of copper leached by Korean Leaching Test (KSLT) is 0.3  $\mu\text{g/g}$  in tailing (MT) from Sangdong mine, which is 30 orders less than that of pH 4.0 and 2 orders less than that of at pH 7.0. For Zn, also, it is observed that the concentration of zinc leached by KSLT is 30 orders less than that of at pH 4.0 and 3 orders less than that of at pH 7.0. The difference between these two results for the tailing from Sangdong mine is due to the pH of leaching solution. As the pH of leaching solution by KSLT is the range from 5.8 to 6.3, which is apart from the leaching condition of this study.

From the leaching test results, in case of tailing, it shows that concentration of heavy metals is largely difference between pH 4.0 and pH 7.0. This suggest that high levels of Zn associated with organic matter may probable be released under the strong acidic condition due to the acid rain or degradation of residual carbon (Ree, et.al., 1995).

#### 4. Conclusions

Fractional composition of metals in soil was depended on kinds of metal, and degree of contamination. Residual and organic fractions of metal were predominant species in all soils, and other fractions existed in small quantity.

In soils, collected from areas where anthropogenic pollution sources found, residual and organic fractions were still dominant species, but these fractions were decreased while fractions of adsorbed, carbonate and Fe-Mn oxide bound were increased, as compared to the uncontaminated soils.

Metal released from mine tailing was highest. Leaching

potential of metals was greater at pH 4.0 than 7.0.

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