

Heavy Metal Speciation in Soils from the Janghang Smelter Area

장항 제련소 지역 토양의 중금속 오염에 대한 환경광물학적 연구

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ABSTRACT : The Janghang smelter is the first lead, zinc and copper smelting facility in Korea which was operated for a half century from 1936 to 1989. The clay minerals and their heavy metal association in the soil profile around the smelter have been studied using XRD, EPMA, SEM-EDS, TEM, EPR and sequential extraction techniques. The soils in A horizon are highly acidic showing pH 4.45. The pH is going up with increasing depth. They have residual water contents of 1.18-1.51 wt %, loss on ignition of 6.32-7.79 wt %, and carbon contents of 0.08-0.88 wt %. Soils consist of quartz, feldspar, muscovite, kaolinite, vermiculite, biotite, chlorite, goethite and hematite in the decreasing abundance. The contents of clay minerals, especially vermiculite and chlorite, decrease with increasing depth. Sequential extraction experiments for the profile samples show that heavy metals (Zn, Cu, Pb, Cd) are highly concentrated in the A horizon of the soil profile as water-extractable (mostly amorphous), $MgCl_2$ -extractable (exchangeable in clay minerals), and organic phases. The heavy metal contents decrease with increasing depth. It suggests that the heavy metals are mainly associated with clay minerals in an exchangeable state. It is also noted that heavy metals are highly concentrated in the manganese and iron oxide phases.

요약 : 장항 지역 토양의 구성 광물과 지권환경 내에서의 중금속 존재 상태에 관한 연구를 위하여 토양 단면 한 곳을 택하여 X선 회절 분석, 광학 현미경, 전자 현미 분석기, 전자 상자성 공명 분광기, 전자 현미경, 연속 추출법 등이 사용되었다. 토양의 일반적인 성질은 다음과 같다. 수소이온 농도는 A층이 4.45이었으며 아래로 내려갈수록 조금씩 증가하였다. 잔류 수분 함량은 1.18-1.51 wt %이었으며 작열감량은 6.32-7.79 wt %였고 탄소함량은 0.08-0.88 wt %를 나타내었다. 토양의 구성 광물은 석영, 장석, 운모, 고령토, 질석, 녹니석 등이었다. 질석의 함량은 깊이에 따라 줄어드는 경향을 보여주었다. 고온 X선회절분석 결과 녹니석이 관찰되었으며 0.2 μm 이하의 입도에서는 명확히 검출되었다. 침철석이나 적철석 등의 산화철이 EDS가 장착된 전자 현미경 분석과 전자 상자성 공명 분광기에서 많이 관찰되었으며 연속 추출 실험 결과 중금속들이 Oxide phase와 밀접한 관련이 있는 것으로 보아 이러한 산화철들이 중금속들과 관련이 깊은 것으로 생각된다. 연속 추출 실험에서는 지권환경 내에서 중금속들이 여러 가지 상태로 들어 있음이 관찰되었다. 중류수에 추출되어져 나온 중금속들은 A층에 많았다. $MgCl_2$ 와 H_2O_2 에 추출되어져 나온 양도 A층이 높게 나타났다. 다른 상태들에서는 큰 특징은 관찰되지 않았으나 대부분의 양이 hydroxyl ammine chloride와 aqua regia에 추출되어져 나왔다.

INTRODUCTION

Soils in Korea are gradually becoming polluted with heavy metals with rapid development of modern industry. Especially, the high pollution is reported from the vicinity of mining or smelter area. The smelting industry has been active in the Janghang area for more than 50 years since 1936. The long continued smelting activity has highly polluted the Janghang area with heavy metals. Many procedures have been proposed to characterize heavy metal pollution for several decades. The sequential extraction has mainly been applied to the characterization of heavy metal pollution of soils (Tessier et al., 1979; Frostner and Calmano, 1982; Gunn et al., 1988; Zachmann and Block, 1994).

Mineralogy and chemistry of soils are important for understanding the speciation of chemical pollution. Recently various techniques such as electron paramagnetic resonance spectroscopy (EPR), secondary ion mass spectroscopy (SIMS) and atomic tunnelling microscopy (ATM) are applied to characterization of chemical behavior of pollution in soil minerals. Synchrotron radiation is also used to understand the chemistry and mineralogy of very fine pollution materials in soils (Henderson et al., 1993).

Especially the clay minerals are likely to react with pollutants in soils because of their characteristic properties such as ion exchange, large surface area, surface negative charge, etc. The intermolecular interactions of pollutants with clay mineral surfaces can be expected to play a crucial role in the subsequent chemical transformations, transport and retention of these contaminants (Siantar et al., 1994). The major objective of this study is to find the distribution patterns of heavy metals in the soil profile and their speciation.

MATERIALS AND METHODS

Geology of the Janghang smelter area consists of Precambrian gneisses and schists, Cretaceous granite and breccia, and Quaternary alluvium and aeolian deposits (Fig. 1, Kim and Shon, 1963). Soil profile samples were taken from the area consisting of gneiss which is about 100 m apart from the smelter chimney. These samples were used for sequential extraction in order to know the heavy metal speciation and distribution with depth.

Profile samples have the numbers from P1 to P8 in the order of increasing depth. P1 and P2 correspond to O and A horizons, respectively. P3 and P4 correspond to B horizon. P5, P6, P7 and P8 correspond to C horizon.

All the soil samples were air-dried and sieved through a 2 mm sieve. For X-ray diffraction (XRD) analysis and electron paramagnetic resonance spectroscopy (EPR), soil samples were gently crushed and powdered by slight grinding with a pestle. Clay fractions were separated by sedimentation and centrifugation methods for XRD and other analyses.

The mineral identification and characterization were investigated by X-ray diffraction analysis (XRD) using a Rikagu Geigerflex X-ray diffractometer with Ni-filtered Cu $K\alpha$ radiation at 40kV/30mA in a continuous scanning mode of scanning speed of $1^\circ 2\theta/\text{min}$.

Soil pH was measured in site as well as in laboratory by the method of 1/2.5 soil/water ratio (Baize, 1988) with a HORIBA portable pH-meter D-12 or a ORION 920A. The instruments were three-point-calibrated with pH 4, 7, and 9 buffer solutions. The pHs were measured in the supernatant liquid in a beaker after a quantity of soil has been shaken in distilled water.

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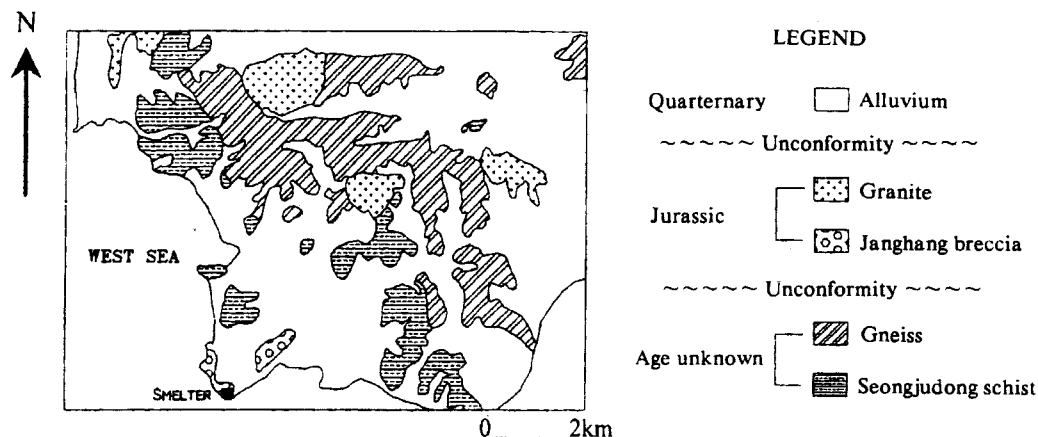


Fig. 1. Geological map of the Janghang area, Seochon, Korea.

Residual water content (RWC) is the loss in weight after drying at 105°C expressed as a percentage of the soil dried in air. It is measured by a simple weighing after drying in the oven long enough (24hrs) to give a constant weight. 1g soil samples were used in this experiment.

The use of divalent barium as a saturating cation is considered by many workers to be more effective than that of monovalent ions (Bain and Smith, 1987). Thus barium saturation method (Gillman, 1979) was used for cation exchange capacity (CEC) measurement.

Electron paramagnetic resonance (EPR) spectra of electronically paramagnetic transition metals in soil samples were obtained at X-band microwave bridge (9.0-9.9 GHz) using a Bruker ESP 300S at room temperature, 77K (liquid nitrogen), and 4K (liquid helium) at the Seoul Branch of the Basic Science Center.

Sequential extraction was performed in order to know mineral phases which contain heavy metals and to quantify the amounts of available heavy metals in each phase. The procedure of Tessier et al. (1979) partly modified was used for sequential extraction in

Table 1. Sequential extraction conditions.

Extraction step (phase)	Solution/ concentration (M)	pH	quantity (ml)	time of extraction (h)
1	deionized water	6.2	10	3
2	magnesium chloride (1)	7.0	10	2
3	NaOAc (1)	5.0	10	12
4	hydroxyl-amine chloride(0.1)	2.0	10	24
5	H ₂ O ₂ (30%)	2.2	10	6
6	aqua regia	<0	10	24

this study. The modified procedure of heavy metal extraction discriminates six phases; water-extractable, MgCl₂-extractable, NaOAc-extractable, hydroxyl ammine chloride (HAC)-extractable, H₂O₂-extractable and aqua regia-extractable phases.

In each experiment, 1g of soils was reacted with a solution in the 50 ml centrifugation tube. The conditions of sequential extraction experiments are summarized in Table 1. The extracted solution of each reaction was filtered (< 0.2μm) to yield a clear solution and were analyzed by induced cou-

Table 2. Some basic properties of soil profile samples

	RWC (%)	LOI (%)	pH in H ₂ O	pH in CaCl ₂	C (%)
P1	1.51	6.83	4.75	4.05	0.88
P2	1.78	6.87	5.38	4.67	0.22
P3	1.60	6.52	5.20	4.45	0.12
P4	1.34	6.42	5.12	4.37	0.09
P5	1.40	7.79	5.08	4.30	0.09
P6	1.30	6.77	5.15	4.42	0.08
P7	1.20	6.52	5.26	4.56	0.08
P8	1.18	6.32	5.45	4.75	0.08

pled plasma-mass spectroscopy (ICP-MS). The water-extractable metals are possibly present as salts or amorphous materials, and the MgCl₂-extractable metals as adsorption to clay minerals, the NaOAc-extractable metals as carbonates, the hydroxyl ammine chloride-extractable metals as oxides, the H₂O₂-extractable metals as organic substances, and aqua regia-extractable metals as stable silicate minerals.

RESULTS AND DISCUSSIONS

Properties of Soils

Some basic properties of profile soil samples were given in Table 2. Residual water content (RWC) is highest in P2 and shows a decreasing tendency with increasing depth. Carbon content also shows a decreasing tendency with depth. C horizon (samples P6-P8) has low content of carbon compared with overlying horizons. Loss on ignition is highest in P5. pHs in surface samples were lowest in the profile. The pHs of the profile show a slightly increasing tendency with depth. The pHs in CaCl₂ show a similar pattern to those in H₂O.

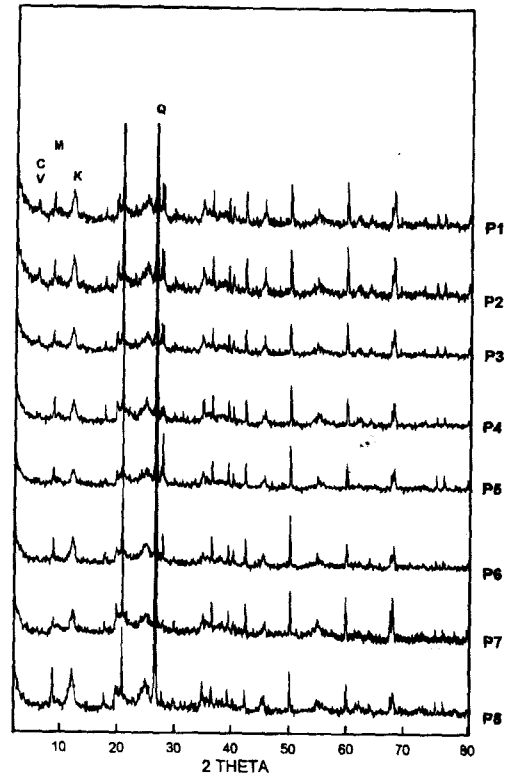


Fig. 2. X-ray diffraction patterns of profile soils (air dried bulk samples). Depth increases from P1 to P8. Q: quartz, K: kaolinite, V: vermiculite, C: chlorite.

Mineralogy of Soils

Soils in the study area are mainly composed of quartz, feldspar, muscovite, kaolinite, vermiculite, biotite, chlorite, goethite and hematite in order of decreasing abundance. XRD patterns of air-dried bulk soil samples of the profile are shown in Fig. 2. The intensity of 14Å peak decreases with depth.

XRD patterns of clay fractions are given in Fig. 3. Kaolinite, vermiculite and mica (illite) are dominant clay minerals. In XRD patterns at room temperature 14Å peak shows a slightly decreasing tendency with depth. Oppositely, 10Å peak shows an increasing tendency with depth. XRD patterns

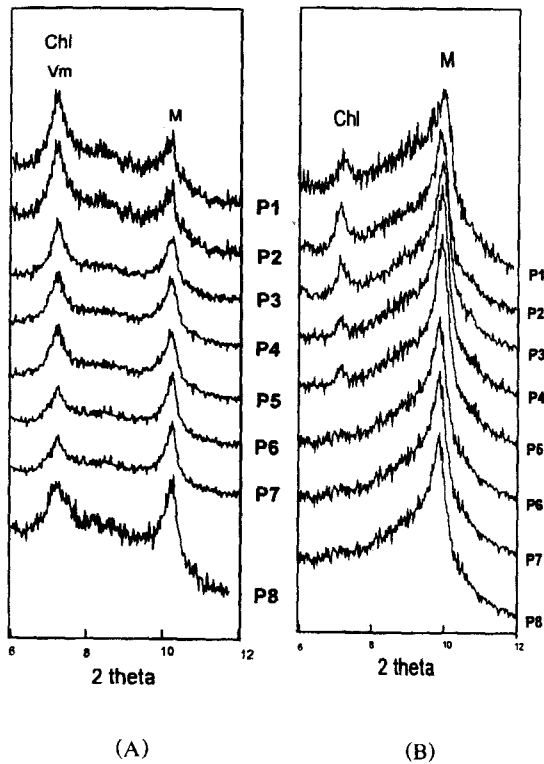


Fig. 3. X-ray diffraction patterns of clay fractions from profile soils. (A) Room temperature (B) more than 550°C.

of clay minerals were obtained at room temperature and 550°C and ethylene glycol intercalation. After heat treatment at 550°C, the intensity of chlorite peak increases toward the soil surface. Jackson (1962) reported hydroxy Al-interlayered clay (Al-chlorite) from the acidic ultisol. Especially, the hydroxy Al-interlayered vermiculite retains its diffraction peaks on heating up to 500°C. But most of near 14Å peak collapsed to 10Å peak. Therefore, pedogenic chlorite can be an evidence that this area has been exposed in acidic environment for a long time.

Speciation of Heavy Metals

The results of all the sequential extraction

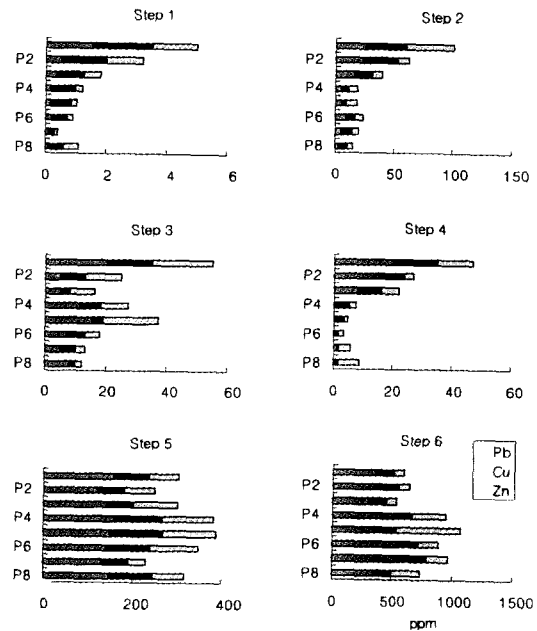


Fig. 4. Sequential extractions of profile soil samples by six steps.

reactions are shown in Fig. 4. Each step has integrated bars of Pb, Zn and Cu. The concentrations of Cd are relatively very low so that they are eliminated. But the relative ratios of Cd concentrations extracted in each extraction steps are shown in Fig. 6.

In the extraction by water (step 1), high heavy metal concentrations were observed in both O (P1) and A (P2) horizons, indicating the presence of relatively large amounts of amorphous materials adsorbing heavy metals. The concentrations of extracted heavy metals are low but they show the similar distribution patterns to those of clay minerals and carbon in the profile. It shows that clay minerals and organic materials are highly associated with water-extractable heavy metals. The concentrations of Zn and Cu were relatively higher than those of other metals.

In the extraction by $MgCl_2$ (step 2), the distribution patterns of heavy metals are almost similar to the above case (step 1). Heavy metals which were extracted in this

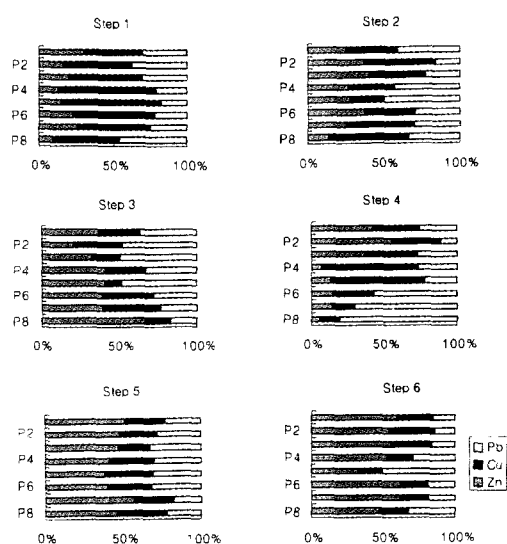


Fig. 5. Percentage ratios of sequential extractions by six steps.

step can be considered as present as exchangeable forms in soils. The concentrations of Pb and Cu were relatively higher than those of other metals.

In the extraction by NaOAc (step 3), high concentrations of Zn and Pb are found in samples P1 and P5. Heavy metals which were extracted in this step can be considered as present as carbonate forms.

In the extraction by H_2O_2 (step 4), high concentrations of heavy metals are detected in O and A horizons. Heavy metals which were extracted in this step can be considered as bound to organic matter. The concentrations of heavy metals in the C horizon are considerably lower than those in overlying horizons. The distribution patterns are similar to those of step 1 and 2. The concentrations of Zn and Cu were relatively higher than those of other minerals.

In the extraction by hydroxyl ammine chloride (step 5), there was no distinguishable tendency with depth. The concentrations of heavy metals in this step are much higher

than those in other steps. Zn, Pb, and Cu are concentrated on samples P4 and P5. SEM-EDS observations show that soil samples P3 and P4 (B horizon) have a lot of Fe-oxides on the surface of soil mineral particles. The heavy metals were also detected from Fe-oxides in the weathered biotite. Thus, it seems that the heavy metals are highly associated with Fe/Mn oxides.

In the extraction by aqua regia (step 6), there was also no distinguishable tendency with depth. The concentrations of heavy metals in this step are much higher than those in other steps. The concentrations of Zn are relatively high and concentrated in the middle depth.

The percentage ratios of all steps from step 1 to 5 in each heavy metal are shown in Fig. 5. In step 1, Cu shows high ratio values at all depths. It means that Cu is highly associated with easily-soluble phase than other metals. In step 2, there is no distinguishable ratio pattern with depth. In step 3, Zn ratio values increase with depth but Pb ratio values decrease slightly with depth. In step 4, Zn ratio values are high in the surface soil samples but Pb ratio value is high at the bottom of profile. It shows that Zn is highly associated with organic bound phases. In steps 5 and 6, there is no distinguishable pattern with increasing depth but Zn ratios are higher than other metals.

The concentration ratio of each extraction step for each heavy metal is shown in Fig. 6. A large part of each heavy metal is extracted in step 5. The relatively high concentrations of Zn are observed in step 4 at the surface soil samples, that is, P1 and P2. The amount of Zn extracted in step 5 decreases with increasing depth. The relatively high concentration of Cd is observed in step 2. It shows that Cd is associated with exchangeable phases in soils. The relatively high con-

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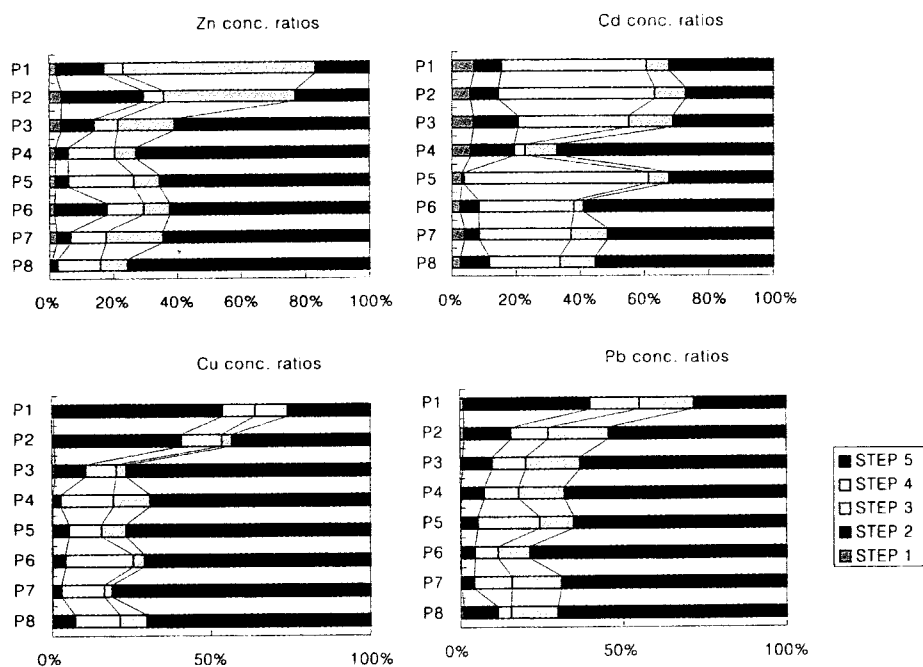


Fig. 6. Concentration ratio of each extraction step for each heavy metal.

centrations of Cu are observed at the surface soil samples, that is, P1 and P2 in step 2. It shows that Cu is associated with exchangeable phases in the surface soil. Pb shows a pattern similar to that of Cu.

Full range X-band spectra of electron paramagnetic resonance (EPR) of randomly oriented powders of profile samples at 4K are shown in Fig. 7. It shows an isotropic transition of Fe^{3+} ions around 1500G ($g=4.3$), which is effectively observed in many glasses and minerals (Calas, 1988). A broad peak near 2300G is probably due to Fe^{3+} ions existing in other electromagnetic environment such as goethite and to ferromagnetism of iron oxides such as magnetite and hematite. Surface coatings and precipitated phases of ferric ion give intense and broad EPR signals (McBride, 1990; Ikeya, 1995). The signal of ferric ion at 800-900G ($g=4.3$) slightly increases with depth. EPR spectra suggest that Fe exists as ferrous state in the form of goe-

thite or ferrihydrite. Fig. 7 also shows EPR spectra of Mn^{2+} ion at 3100-3600G. The Mn^{2+} spectra consist of characteristic six groups of hyperfine structure (HFS) components. The patterns of HFS of Mn^{2+} ions are changed with depth, indicating that surrounding ion environment of Mn^{2+} ion varies with depth. Line widths of HFS decrease with depth. Furuhashi and Kuwata (1969) have reported that the line widths of HFS of hydrated Mn^{2+} are broader on the exchange sites of clay minerals than in bulk solution. Thus, it seems that Mn^{2+} ions in C horizon (P7 and P8) are less hydrated than those in overlying horizons. HFS structures of Mn^{2+} is rather strong in A horizon (P1). It suggests that Mn is present mainly as Mn^{2+} showing tendency of hydration toward the surface. The splitting of spectrum of Mn^{2+} ion is due to the spectrum of Cu^{2+} ions at 3200G. The contents of Cu^{2+} ions are comparatively high in A and B horizons.

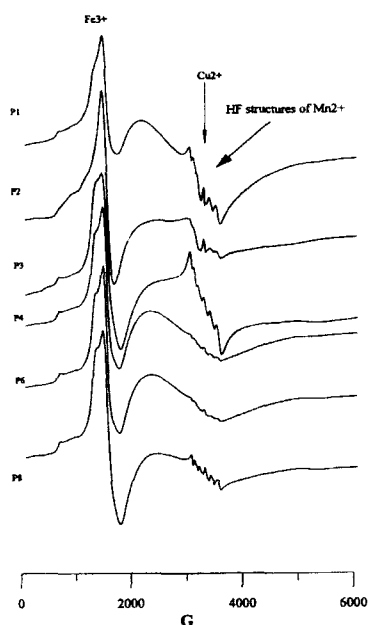


Fig. 7. Full X-band EPR spectra of profile soil samples at 4K.

CONCLUSIONS

Soils in the vicinity of the Janghang smelter area are highly acidized and polluted with heavy metals. The profile soils consist of quartz, feldspar, muscovite, kaolinite, vermiculite, biotite, chlorite, goethite and hematite in the decreasing abundance and the contents of vermiculite and chlorite decrease with depth.

The heavy metals are predominantly concentrated in the water-extractable amorphous materials and $MgCl_2$ -extractable clay material. They show a decreasing tendency toward depth. It suggests that heavy metals are mainly concentrated in clay minerals in an exchangeable state in the A and B horizons of the soil profile.

ACKNOWLEDGMENT

This work was supported by the Interna-

tional Cooperative Research Program between Korea and United Kingdoms (KOSEF 96-0401-003-2), the Korea Science and Engineering Foundation.

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