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Arsenic, Cadmium, Chromium, Copper, Lead, and Zinc Contamination in Mine Tailings and Nearby Streams of Three Abandoned Mines from Korea

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There are more than 1,000 abandoned mines in Korea, entailing considerable amounts of waste materials such as rock, tailings and slag. In many cases, mine tailings, the major solid wastes, have been disposed to nearby valleys and cultivated lands without appropriate treatment. Most of these tailings have been exposed to physical and chemical weathering, leading to high concentrations of As and heavy metals in the immediate vicinity of mine and consequently causing to contaminate surrounding soils, groundwater and streams (Castro-Larragoitia et al. 1997; Jung 2001; Lee et al. 2001; Shu et al. 2001). Up to now, many studies have been conducted to determine the behaviors of As and heavy metals in the mine tailings and to assess their impact to human and organisms (Lee et al. 2001; Riba et al. 2002).

The characteristics of As and metals, such as toxicity and bioavailability, depend not only on their total concentrations, but also on their mobility and reactivity with other components in the environment. The mobility of heavy metals in soils is usually examined by extraction using solutions with different chemical properties (Abollino et al. 2002). Our primary goal in the present study is to investigate the distributions and behaviors of arsenic and heavy metals (Cd, Cr, Cu, Pb and Zn) in and around mine tailings. Experiments were conducted to measure the total concentrations of arsenic and heavy metals in the tailings and nearby streams. After leaching of the tailings in water, the concentrations of As and heavy metals in the leachates were determined. The values of several chemical parameters were also measured. Finally, we investigated the relations between the distributions of heavy metals and the chemical parameters in and around the tailings. It is expected that this study would be helpful for better prediction of the mobility and reactivity of contaminants in mine areas.

MATERIALS AND METHODS

For this study, six samples of mine tailings were obtained from three abandoned mines (Jingok, Cheonbo and Sino mines) in Korea (December 2000). The detailed information about the mines and sampling has been described in a previous paper (Kim et al. 2002). At each mine, two 1 kg soil samples were collected at 20 cm depth from two different sites. The samples were dried using a freeze-drier for 3-4 days and homogenized by thorough mixing. Subsequently the samples were

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stored in a freezer until further analysis. Water samples were collected from shallow streams around the mine tailings. After measuring dissolved oxygen (DO) and pH, the water samples were filtered through 0.45 μm membrane filters and then acidified with HNO_3. The water samples were stored in a cooler in the field and in a refrigerator in the laboratory until analyzed. The concentrations of dissolved arsenic and heavy metals in stream water were measured using an atomic absorption spectrometer (AAS).

The geological characteristics of the mine tailings were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The contents of organic materials in the mine tailings were determined by the method of "Loss on Ignition". After digesting the tailings sequentially with HNO_3, HCl and H_2O_2, the total concentrations of As, Cd, Cr, Cu, Pb, Zn, Fe, Mn and Al were determined using AAS.

Thirty grams of each sample (sieved through a 2mm sieve) and 150 mL of deionized water were placed in a 250 mL Erlenmeyer flask. Then, the six flasks were shaken using a platform shaker (160 rpm, 27°C) for one hour. The suspended mixtures were filtered through 0.45 μm pore size membrane filters. The concentrations of arsenic and heavy metals in the leachates were determined using AAS, whereas those of anions (Cl^-, F^-, NO_3^-, NO_2^- and SO_4^{2-}) were using an ion chromatography (IC). At the same time, pH and DO of the leachates were also determined. Arsenic species in the leachates were separated using an ion exchange method (Kim et al. 2002).

RESULTS AND DISCUSSION

The mineralogy of the tailings was dominated by quartz. The XRD and SEM analyses revealed the presence of sulfide minerals such as pyrite (FeS_2), arsenopyrite (FeAsS), sphalerite ((FeZn)S), galena (PbS) and chalcopyrite ($CuFeS_2$) (Figure 1).

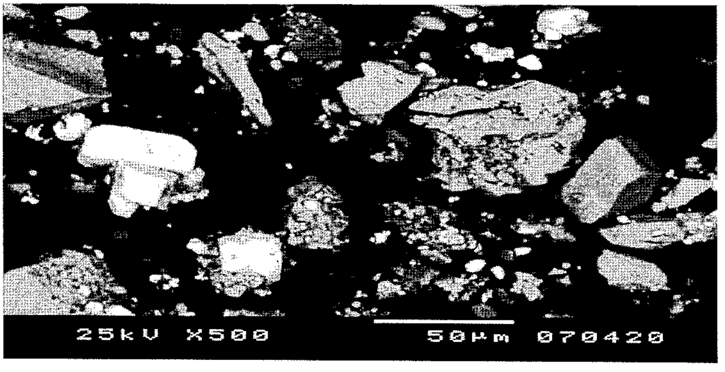

Figure 1. SEM (backscattered electron) of Sino 2 (SO 2) sample: bright spots represent sulfide minerals containing Fe, Zn, Cu, Pb and S.

Table 1 shows the total concentrations of arsenic and heavy metals (Cd, Cr, Cu, Pb, Zn, Fe, Mn and Al) in the mine tailings and their leaching rates in water. The results indicated that the mine tailings were heavily polluted with heavy metals and the total concentration of each metal was diverse. The total concentrations of elements in the tailings were up to 62350 mg/kg As, 43 mg/kg Cd, 4.7 mg/kg Cr, 599 mg/kg Cu, 51400 mg/kg Pb, 3850 mg/kg Zn, 40 wt.% Fe, 21400 mg/kg Mn, and 7850 mg/kg Al. The concentrations of arsenic, lead and iron were much higher than those of the other metals. There are high correlations between total iron and arsenic (R^2=0.95), and between total iron and cadmium (R^2=0.94) in the mine tailings, suggesting that Fe (hydro)oxides would be important in controlling As and Cd adsorption reactions. Mn and Al (hydro)oxides, and organic materials less contributed to adsorption. The contents of the organic materials in the tailings samples were very low, for example 0.7% at maximum for Jingok and Cheonbo samples. In the present study, therefore, the effects of organic materials on the arsenic and metal adsorption were negligible.

In all the six samples, the soluble As and metals in water occupied only minor fractions of the total As and metal concentrations in the mine tailings. The leaching rates were mostly in the range of 0 to 3.9% except for several exceptionally high values (5.3-19.4%). The fact that the leaching rates were in such a wide range would be related to several factors, including the adsorption of As and metals onto Fe (hydro)oxides and the formation of insoluble sulfide compounds (Bowell et al. 1994; Raven et al. 1998; Dong et al. 2000). Significant correlations between the concentrations of As and heavy metals in the leachates and those in the mine tailings were not found. The concentrations of arsenic (average 13.5 mg/L and highest 45.6 mg/L) and zinc (average 28.3 mg/L and highest 136 mg/L) in the leachates were much higher than those of the other metals (Figure 2). It was found that the major arsenic species in leachates were As(V) (63-99%), suggesting that As(V) should be the predominant arsenic species in the mine tailings under oxic conditions.

The values of pH and DO, and the concentrations of fluoride, chloride, nitrite, nitrate and sulfate in the leachates of mine tailings have been shown in details in a previous paper (Kim et al. 2002). The leachates in all the soil samples were in the acidic condition (pH=1.9-5.5) except for Cheonbo 2 sample (pH=7.4). Sulfate was the dominant anion in the leachates whereas the concentrations of the other anions were very low (0-1.7 mg/L). The values of DO were relatively low (2.9-5.7 mg/L). Neither correlations between the chemical parameters and dissolved metal concentrations nor between the anion concentrations and dissolved metal concentrations was found.

Table 1. Concentrations of arsenic and heavy metals in mine tailings and their leaching rates in water

	Concentrations of arsenic and metals in mine tailings[a]								
	As	Cd	Cr	Cu	Pb	Zn	Fe	Mn	Al
JG[b] 1	3795±7.1[e]	3.9±0.2	2.5±0.1	460±22	7753±468	2636±220	6.6±0.02	21400±141	7850±750
JG 2	3015±63.6	5.0±0.4	4.7±0.5	111±7.3	3023±65	2663±197	5.2±0.06	14050±71	6450±187
CB[c] 1	2325±21.2	ND	3.3±0.9	13.5±0.6	223±55	34.5±4.7	1.9±0.02	42.5±0.7	2420±212
CB 2	880±14.1	0.25±0.06	3.7±0.2	16±2.5	344±7.7	274±11	1.16±0.08	123±1.4	2515±162
SO[d] 1	62350±495.0	42.5±0.35	2.7±0.04	364±1.4	51400±566	3500±0	33.2±0.35	12.4±1.0	4310±184
SO 2	57750±919.2	36.5±0.49	1.48±0.04	599±3.54	567±4.24	3850±71	40.1±0.35	3.1±0.49	758±11.3

	Leaching rates in water (%)								
	As	Cd	Cr	Cu	Pb	Zn	Fe	Mn	Al
JG 1	0.0017	8.28	-	0.51	-	3.38	-	0.37	0.04
JG 2	0.059	0.99	-	0.03	-	1.79	-	0.07	0.02
CB 1	0.032	-	-	1.33	0.10	3.33	0.15	2.94	0.05
CB 2	0.089	-	-	0.50	-	0.02	-	0.07	0.04
SO 1	0.37	17.96	5.71	2.60	0.03	19.43	0.84	5.34	3.37
SO 2	0.3	1.52	1.69	1.82	3.44	0.79	0.2	3.89	2.37

[a] Unit = mg/kg except for Fe (wt. %)
[b] Jingok mine, [c] Cheonbo mine, [d] Sino mine
[e] average±standard deviation, ND = not detectable, Blank = not calculable

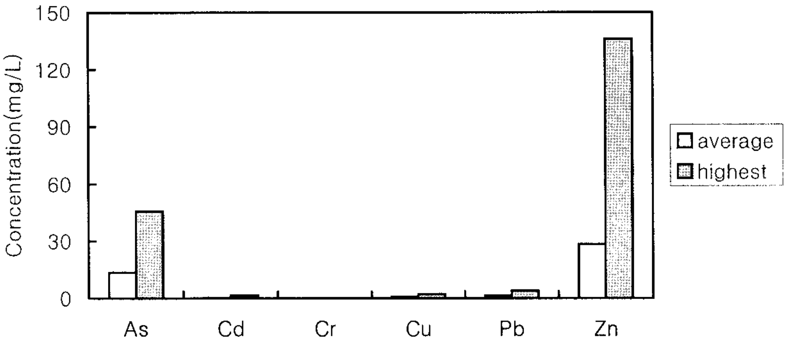

Figure 2. Average and the highest concentrations of arsenic and heavy metals in leachates of mine tailings.

Table 2 shows the concentrations of dissolved arsenic and heavy metals (Cd, Cr, Cu, Pb and Zn) in the streams. The stream water was under the acidic to neutral condition of pH=5.3-7.5 and in the range of DO between 8.2 mg/L (10.8°C) and 12.3 mg/L (2.3°C). The concentrations of arsenic (42-915 μg/L) and zinc (0.23-9.1 mg/L) in the streams were noticeably high compared to the other metals. These results are consistent with those in the leachates of mine tailings. The arsenic concentrations in the stream water and leachates exceeded the current maximum contaminant level (MCL) of U.S. Environmental Protection Agency (USEPA) in drinking water, 50 μg/L. From the leaching experiments and the analysis of stream water samples, it is expected that the stream and groundwater around the mine tailings would be heavily contaminated with arsenic and zinc during the repetitive long rainy season.

The arsenic speciation was not conducted with the water samples in the present study. Nevertheless, it is assumed that, based on the values of almost saturated DO, the major arsenic would be As(V) in the stream water. The concentrations of other metals (Cd, Cr, Cu and Pb) in the water samples were undetectable or low.

Table 2. Concentrations of dissolved arsenic and heavy metals in stream water around mine tailings

	As	Cd	Cr	Cu	Pb	Zn
JG[a]	42.1±2.7[d]	ND	ND	0.7±0.2	ND	230±0.0
CB[b]	915.2±5.0	0.7±0.1	35.1±1.8	23.9±1.0	32.7±1.6	240±0.0
SO[c]	73.2±1.5	70.0±0.0	ND	2.2±0.2	ND	9100±141

[a] Jingok mine, [b] Cheonbo mine, [c] Sino mine
[d] average±standard deviation, Unit = μg/L, ND = not detectable

The main sources of pollutants in the study area would be sulfide minerals containing arsenic and heavy metals. The geochemical processes occurring in the mine tailings of the study area would consist of a combination of reactions including dissolution of sulfide minerals, sulfide oxidation and adsorption/desorption. It is likely that all these processes have a certain extent of influence on the high concentrations of arsenic and heavy metals in stream and groundwater. The degree of pollution and risk, and the physicochemical characteristics of each pollutant are diverse in the area of mine tailings. Therefore, for efficient reclamation of the polluted sites, further investigation should be conducted to study the distribution and mobility of arsenic and each heavy metal in water as well as in mine tailings.

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