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Heavy metal speciation trends in mine slime dams: A case study of slime dams at a goldmine in Zimbabwe

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Heavy metal speciation trends in the slime dams at a typical gold mine in Zimbabwe were studied using a six-step sequential extraction technique to give six fractions, namely, the exchangeable, acid soluble, easily reducible, moderately reducible, oxidizable and residual fractions. The elements studied include Cd, Co, Ni, Cu, Zn, Cr, Fe and Mn. Cadmium was found mainly in the acid soluble fraction, and to a lesser extent in the exchangeable and easily reducible fractions. For the other elements, speciation trends within the slime dams appear to depend, in the main, on the stability of metal cyano complexes formed during the cyanide extraction process, and the ease with which the metals co-precipitate with Mn oxides and/or CaCO₃. For Fe speciation trends depend mainly on the pH within the slime dam.

Key words: Heavy metal speciation, heavy metal mobility, slime dam, mine tailings, sequential extraction.

INTRODUCTION

Mining is a major activity in Southern Africa. The result is that the region is home to thousands of mine solid waste dumps. Release of toxic metals from such solid waste dumps depends on the mobility of the elements within the dumps. Transformations in the chemical form of toxic metals and other toxic substances in these mine solid waste dumps will affect the mobility and bioavailability of such toxic substances (Tessier et al., 1989; Sager, 1992). There is therefore need to study the speciation trends of toxic metals in mine solid waste dumps, with the view of understanding how the release of such toxic metals from mine solid waste dumps can be controlled. Although several workers have studied the impact of mine solid waste dumps in the region on the quality of surrounding surface and ground water (Rosner and van Schalkwyk, 2000; Winde and Sandham, 2004; Zaranyika et al., 1994, 1997; Rafiu, 2007; Nsimba, 2009), there are no reports on speciation studies of trace metals within the mine solid waste dumps themselves.

Speciation of metals in soils, sediments and solid wastes is often studied using sequential extraction techniques whereby the target metals are fractionated into several fractions using extractant solutions of increasing strength (Tessier et al., 1979). Several such sequential extraction schemes have been described (Chester and Hughes, 1967; Tessier et al., 1979; Gibson and Farmer, 1983; Brown et al., 1984; Gibson and Farmer, 1986). The technique has been used to study the speciation of heavy metals in soils, street sweepings and urban aquatic sediments, lake sediments, pelagic sediments, semiarid soils, dredged sediment derived surface soils, and solid waste materials (Gibson and Farmer, 1986; Kabala and Singh, 2000; Lu et al., 2003; Mehra et al., 1999; Wilbur and Hunter, 1979; Banerjee, 2003; Tessier et al., 1989; Vuorinon and Carlson, 1985; Chester and Hughes, 1967; Navas and Lindhorfer, 2003; Singh et al., 1998; Flyhammar, 1997). The technique has also been used to study the speciation, mobility and bioavailability of radionuclides (Riise et al., 1990; Salbu et al., 1994; Blanco et al., 2004).

The aim of the present work was to study the speciation trends of selected heavy metals in the slime dams of a typical gold mine in Zimbabwe, with the view of

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Table 1. Sequential extraction scheme used*.

Fraction	Extractant	Shaking Time (h)	Temp(°C)	Designation
F1	1 M NH ₄ AC, pH 7	8	RT**	Easily exchangeable
F2	1 M CH ₃ COONa, pH 5	15	RT	Acid soluble
F3	0.1 M NH ₂ (OH)Cl/0.2M HNO ₃	1	RT	Easily reducible
F4	1 M NH ₂ (OH)Cl/25% CH ₃ COOH	15	RT	Reducible
F5	30% H ₂ O ₂ /0.02 M HNO ₃	6	85	Oxidizable
F6	HClO ₄ /HF			Residual fraction

*Source: Gibson and Farmer (1986), **RT = room temperature.

understanding how such speciation trends affect the mobility of the metals within the slime dams. The elements studied include Cr, Co, Ni, Cu, Zn, Cd, Fe, and Mn. Major trends studied are speciation as a function of time, speciation as a function of depth in the slime dam, inter-conversion between speciation fractions, and inter-element speciation relationships.

MATERIALS AND METHODS

The gold mine selected for the study is situated about 50 km north of Harare. The ore mined consists of pyrite (FeS₂), pyrrhotite (Fe_{1-0.8}S), and arsenopyrite (FeAsS) as the major minerals, and chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄) and pyrolucite (MnO₂) as minors. The ore is crushed and milled to fine particles, then treated with alkali cyanide and compressed air to dissolve the gold (Puddephatt, 1978). The solution is filtered, and the tailings are treated with lime and ferrous sulphate to complex any excess cyanide ion in the slurry before being discharged onto slime dams. Slime dam soil samples were collected from two slime dams, the current slime dam (or CSD) still receiving tailings, and an old slime dam (OSD) no longer receiving tailings, using a soil corer 15 cm in diameter. In the current slime dam (CSD), samples were collected from three points approximately 30 m apart. At each sampling point, samples were collected at three depths of 15, 50 and 100 cm from the surface. The Old Slime Dam (OSD), about 10 m high, was in the process of being reworked, and samples were collected at the surface, about 100 cm, and at the bottom. The samples were collected into clean plastic bags previously soaked in ultra-pure dilute nitric acid (Merck, Germany) overnight and then rinsed with distilled de-ionized water. All soil samples were tightly sealed and immediately taken to the laboratory where they were stored in a refrigerator prior to analysis.

For analysis soil samples were thawed then partially dried in an oven at 80°C in order to evaporate off most of the entrapped water. Analysis of the soil was done after sequential extraction into 6 fractions after Gibson and Farmer (1986). An aliquot of 1 g of the ground soil was placed in an Erlenmeyer flask and 10 ml of 1-M ammonium chloride solution added. The flask was stoppered and shaken on a mechanical shaker for 1 h, after which the sample was centrifuged at 4000 rpm for 10 min. The supernatant solution was transferred to a plastic vial for storage (Fraction I (F1), Table 1). To the residue in the centrifuge tube, 10 ml of de-ionized water were added, the mixture centrifuged again and the supernatant combined with the first extract.

For subsequent fractions the residue after extraction of the preceding fraction was washed into a clean Erlenmeyer flask with a solution of the appropriate reagent (Table 1), and the extraction

carried out as given in Table 1. Analytical grade reagents were used to prepare standard solutions for all the analyses carried out. The results obtained, expressed as percentages of the sum of all the six fractions, are shown in Figure 1 in bar graph form for samples from the current slime dam, while Figure 2 shows the percentages for each fraction at each depth sampled in the old slime dam. The use of percentages eliminates variations in the quantities of the metals measured caused by variations in the composition of the tailings deposited on the slime dam at different times. Figure 3 shows bar graphs and standard error bars, for the mean total element concentrations in the 1 m surface layers of the two slime dams. Table 2 shows the mean total element concentrations at the three depth levels sampled in the old slime dam. Statistical calculations were done using Minitab for Windows Release 10 statistical package (Minitab, 1994).

The efficiency of the sequential extraction technique was tested by performing total element metal determination using the acid digestion method, and comparing the result to the total element obtained by the sequential extraction method. The results obtained for the efficiency of the sequential extraction technique, expressed as %recovery, are shown in Figure 4. The pH of the slime dam soil was measured using a pH meter after shaking a 2 g aliquot of the ground sample with 20 ml of deionised distilled water (McLean, 1982). The pH values obtained for the various samples are shown in Table 3.

RESULTS AND DISCUSSION

pH within the slime dams

Tailings are deposited on the slime dams at a minimum pH of 10.5. Table 3 shows that pH in the surface layers of the current slime dam is very variable, ranging from an average of 6.28 at Sampling point 2 to 8.14 at Sampling point 3. This is probably related to the time elapsed since the slime effluent discharge was directed at each sampling point. The tailings discharge is rotated so that there is an even build up of the slime dam. It is also apparent from Table 3 that there is a well defined pH increase with depth at Point 2 from 4.95 at the surface to 7.94 at 1-m depth. On the other hand the pH at Points 1 and 3 appears to be fairly uniform.

Another cause of the variations in pH is probably variations in the composition of the tailings discharged, especially its sulphide content and lime content. The ore being processed at any one time determines the sulphide

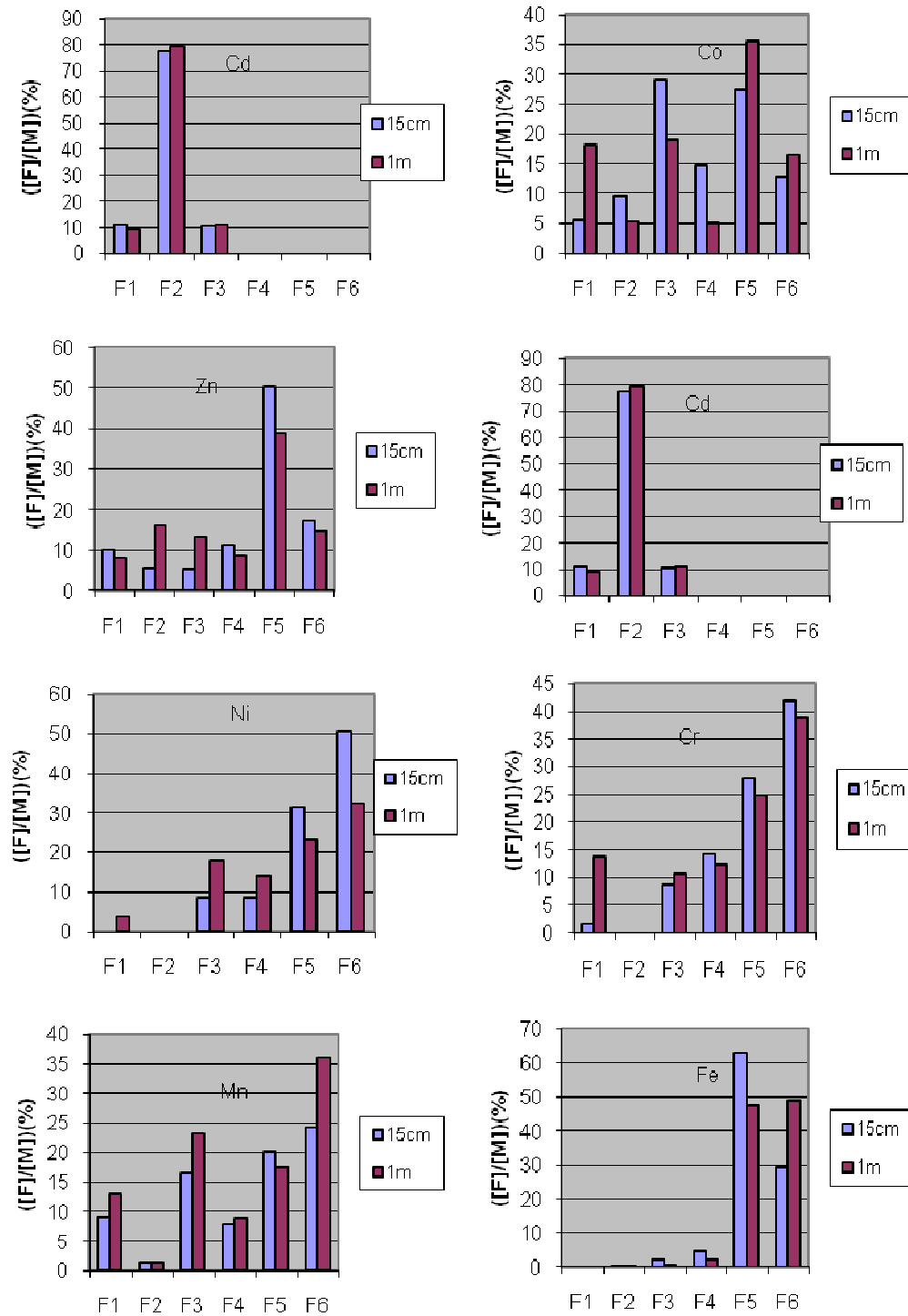


Figure 1. Speciation of Cd, Cu, Zn, Co, Ni, Cr, Mn and Fe in the current slime dam: [F] = concentration of speciation fraction; [M] = total element concentration.

content. The old slime dam shows a drastic pH drop from 6.56 at the surface to about 3.16 at approximately 1 m depth, and 2.21 at its base. This is attributed to the accumulation of acidic conditions at the base of the dump as a result of sulphide oxidation in the surface layers.

Total element concentrations

From Figure 3, it is apparent that for Ni, Cu, Zn, Cd and Co, total element concentrations in the 1 m surface layer of the current slime dam are much lower than those in the

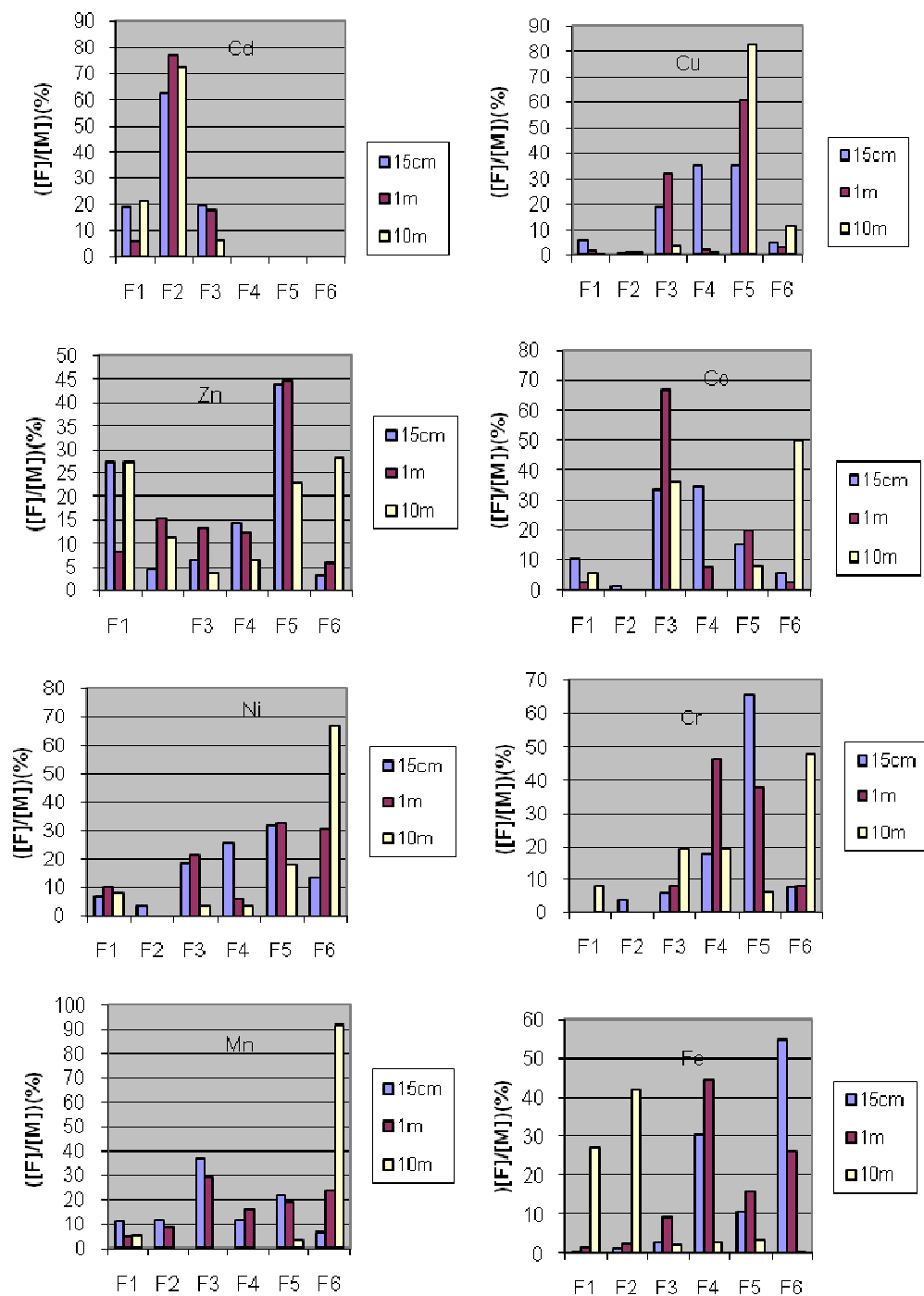


Figure 2. Speciation of Cd, Cu, Zn, Co, Ni, Cr, Mn and Fe in the old slime dam: [F] = concentration of speciation fraction; [M] = total element concentration.

old slime dam, while the reverse is true for Cr, Mn and Fe. The low concentration of Fe, Mn and Cr in the surface 1 m layer of the old slime dam is attributed to leaching that has taken place since the time that deposition of tailings was discontinued. A possible explanation for the fact that the concentrations of Ni, Cu, Zn, Cd and Zn are higher in the old slime dam is that the

current ore being processed in the plant is low in these elements compared to the ore that was being processed when tailings were being deposited on the old slime dam. Total element data for the old slime dam in Table 2 shows that for Cd and Cr, concentrations drop steadily with depth, while for Mn, Co, Cu, and Ni concentrations drop in going from the surface to the 1 m level, then

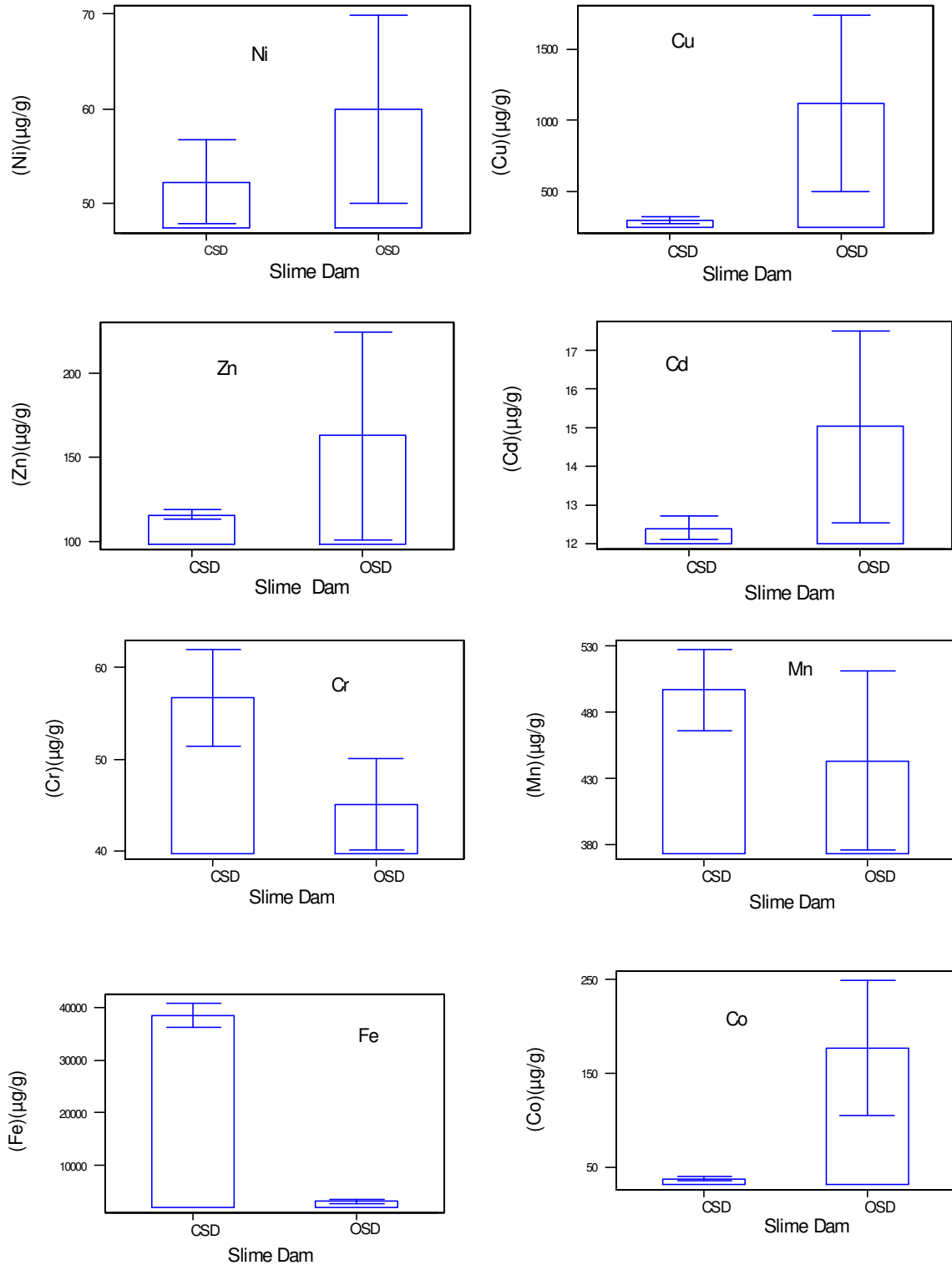


Figure 3. Mean total element concentrations in the 1m surface layer of the current and old slime dams: (a) Cr, Mn, Fe and Co; (b) Ni, Cu, Zn and Cd.

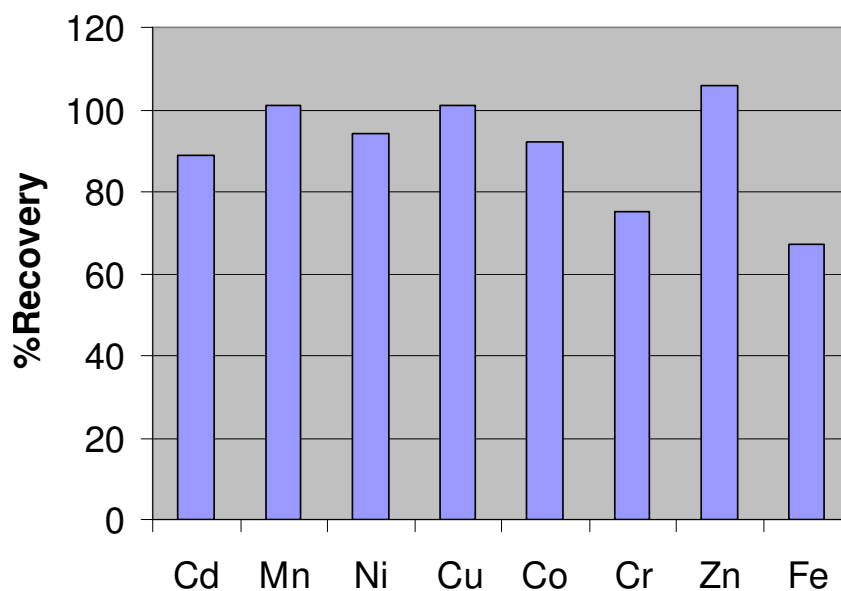
increase at the base of the slime dam. Zinc concentration drops in going from the surface to the 1 m level, then

levels off.

On the other hand, Fe shows a steady increase with

Table 2. Mean total element concentrations ($\mu\text{g/g}$) in the old slime dam ($n = 3$).

Element	Surface	1 m depth	Base (10 m)
Cd	17.6 \pm 0.1	12.3 \pm 0.3	13.5 \pm 0.4
Mn	512 \pm 11	375 \pm 20	650 \pm 10
Ni	75 \pm 1	50.0 \pm 0.8	70 \pm 5
Cu	1750 \pm 100	500 \pm 148	525 \pm 6
Fe	1975 \pm 100	2500 \pm 300	3500 \pm 400
Co	250 \pm 5	105 \pm 2	135 \pm 4
Cr	95 \pm 10	50 \pm 6	40 \pm 4
Zn	225 \pm 20	100 \pm 6	100 \pm 4

**Figure 4.** Sequential extraction recovery efficiency.

depth, probably due to the conversion of Fe(II) cyano complex to insoluble Fe(III) oxides. Table 2 further shows that at the surface of the old slime dam, the concentrations of the elements studied decrease in the order: Fe > Cu > Mn > Co > Zn > Cr > Ni > Cd. At the 1 and 10 m levels, the order remains the same, except for Cr and Ni which are approximately equal at the 1 m level, while Ni > Cr at the base of the slime dam.

Extraction efficiency

Sequential extraction percentage recoveries of 89 \pm 3, 101 \pm 1, 94 \pm 8, 101.7 \pm 0.2, 67 \pm 44, 92 \pm 6, 75 \pm 5 and 106 \pm 2 were obtained for Cd, Mn, Ni, Cu, Fe, Co, Cr and Zn respectively, (Figure 4). The poor recovery for Fe is attributed to filtration loss of colloidal Fe hydroxides during the sequential extraction.

Speciation trends in the current slime dam

Figure 1 shows the percentage of the various fractions for the different elements in the form of bar graphs. Examination of this figure shows that the following groups of elements show roughly similar trends in speciation: (a) Ni, Cr, Mn and (b) Cu, Zn, Co. Cadmium and Fe show unique speciation patterns.

Cadmium

Cd in the surface layers of current slime dam is available mainly in the acid soluble fraction, F2, at 80%, and the balance as the exchangeable fraction, F1, and the fraction associated with Mn oxides, F3. It is interesting to note that, although other elements are available in the residual fraction, Cd is not found in the residual fraction. It

Table 3. pH in the current slime dam and the old slime dam.

Slime dam	Depth (m)	SP1	SP2	SP3
Current	0	7.25	4.95	8.07
	0.5	6.88	5.96	8.20
	1.0	6.75	7.94	8.16
	Mean	6.96	6.28	8.14
Old	1	6.56		
	4	3.16		
	10	2.21		

SP = sampling point.

would appear from this that Cd is completely leached out of the mineral fraction during the ore processing and gold extraction process. An alternative explanation is that Cd is introduced into the slimes through the chemicals used in the gold extraction process or the treatment of the tailings prior to their discharge on the slime dam. The predominance of Cd in the acid soluble fraction is attributed to co-precipitation by CaCO_3 (Jones and Jarvis, 1981). There are no significant speciation differences between the 15 cm and 1 m samples.

Manganese, nickel and chromium

This group comprises Group 6B, 7B and 8B elements. For this group the residual fraction, F6, is the highest, while the acid soluble fraction, F2, is the lowest at 1% for Mn and Ni, and zero for Cr. For all three elements, the oxidizable fraction, F5, is the next highest fraction, followed by the moderately reducible fraction, F4, for Cr, and the easily reducible, F3, for Mn and Ni. The exchangeable fractions for the three elements are 11, 5 and 10% respectively for Mn, Ni and Cr. The very low levels of the acid soluble fraction suggest that these elements are not co-precipitated by CaCO_3 .

Copper, cobalt and zinc

The oxidizable fraction, F5, is the most prevalent for Cu, Co, and Zn. This group differs from the Mn, Ni and Cr group in the levels of the acid soluble fraction which are higher at 3, 10 and 13% respectively for Cu, Co, and Zn, suggesting co-precipitation by CaCO_3 to a limited extent. Results from soil leaching experiments with slightly acidic buffers show that, in most cases, carbonates can take up only 1 to 6% Cu (Sager, 1992).

Iron

For Fe only the oxidizable fraction, F5, and the residual

fraction, F6, are found at 52 and 47% respectively. The content of iron sulphide minerals in the ore is high. Since FeSO_4 is added to the tailings to complex any excess cyanide ion, the absence of fractions 1 to 4 (only 1% of F4 is found), suggests that the $\text{Fe}_2[\text{Fe}(\text{CN})_6]$ complex formed shows in fraction 5.

All the metals studied form complexes with the CN^- ion (Moeller, 1963; Cotton and Wilkinson, 1972a), and we would also expect these to appear in Fraction 5. This may explain the high levels of this fraction for the elements Mn, Ni, Cr, Cu, Co and Zn. On this basis we conclude that the cyanide complex of Cd is not stable under the conditions found in the slime dam.

Speciation trends in the old slime dam

In discussing speciation trends in the old slime dam attention is focussed on (a) comparison of speciation trends in the surface layers of the current slime dam and the old slime dam in order to highlight the effect of time on speciation trends in the surface layers of the slime dams, (b) speciation trends as a function of depth in order to highlight the effects of leaching and change in pH, (c) inter-conversion between speciation fractions, and (d) inter-element speciation relationships.

Cadmium

For Cd, comparison of Figures 1 and 2 shows very little difference in the speciation pattern in the surface layers of the slime dams. The acid soluble fraction, F2, is still the highest in the old slime dam, although there is a drop from 80 to 62%. This is accompanied by increases in the exchangeable and moderately reducible fractions, F1 and F3 respectively, to 19% from 9 to 10%. The increase in F1 and F3 in going from the current slime dam to the old dump suggests slow release of Cd from CaCO_3 precipitates, possibly via replacement by Ca.

Figure 5 shows that the profiles of the F2 and F3 fractions are parallel, suggesting very little or no

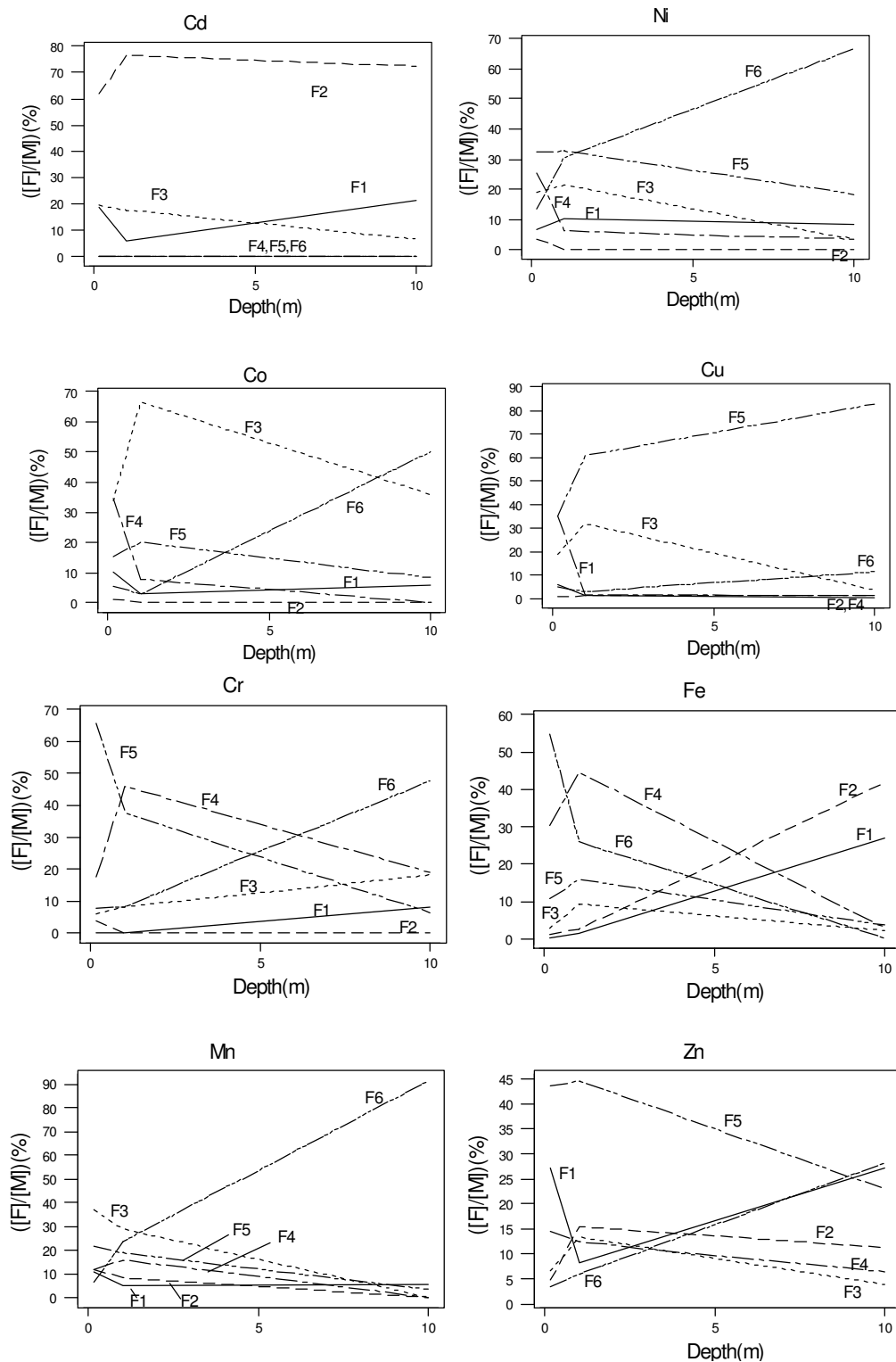


Figure 5. Speciation as a function of depth in the old slime dam: [F] = concentration of speciation fraction; [M] = total element concentration.

interconversion between these two fractions. The profiles of the F1 and F2 fractions are, on the hand, mirror

images, as are the profiles of F1 and F3, suggesting interconversion between these pairs of speciation

Table 4. Pearson's correlation factor* for residual fractions.

	F6(Ni)	F6(Cu)	F6(Co)	F6(Zn)	F6(Cr)	F6(Mn)
F6(Cu)	0.861					
F6(Co)	0.932	0.987				
F6(Zn)	0.975	0.953	0.989			
F6(Cr)	0.951	0.976	0.998	0.996		
F6(Mn)	0.992	0.919	0.971	0.995	0.983	
F6(Fe)	-0.973	-0.720	-0.823	-0.897	-0.854	-0.935

* Minitab (1994).

fractions. Sorption of Cd by hydrated CaCO_3 has been shown to be reversible (Sager, 1992). At the surface (15 cm) the levels of F1 and F3 are approximately equal. At 1 m depth $\%F3 > \%F1$, probably due to leaching of F1, or conversion of F1 to F3 via co-precipitation with Mn oxides. At 10 m $\%F1 > \%F3$. This can be due to leaching of F1 to the base of the slime dam, coupled with conversion of F3 to F1 as a result of the increased acidic conditions at the base of the slime dam.

Iron

For Fe the residual fraction is the highest in the surface layers of the old slime dam, followed by F4, then F5, F3 and F2. The exchangeable fraction, F1, is negligible. In the middle of the slime dam, F4 is the highest, followed by F6, then F5, F3, F2 and lastly F1. In the bottom layers, F6 becomes negligible, while F2 is now the highest, followed by F1. Fractions F5, F4 and F3 are very low at 4, 3 and 2% respectively. From Figure 5 the major speciation change in the surface layers, 15 cm to 1 m, with time is the weathering of the residual fraction F6 to yield the oxidizable Fraction F5, and fractions associated with Mn and Fe oxides, that is, F3 and F4 respectively. Between 1 and 10 m the mineral bound fraction, F6, the oxidizable fraction F5, and the oxy-hydrates fractions F3 and F4, are all converted to the acid soluble fraction, F2, and the exchangeable fraction, F1, as a result of the increased acidic conditions at the base of the slime dam. The net result is the build-up of the acid soluble and the exchangeable fractions at the base of the slime dam.

Cobalt

From Figure 5 the major speciation change for Co with time in the surface layers, 15 cm to 1 m, is the conversion of the fraction associated with Fe oxy-hydrates, F4, to the fraction associated with Mn oxy-hydrates, F3. For the elements studied, Co is unique in this respect, that is, the increase in the fraction associated with Mn oxides. The association of Co with Mn oxides has been reported

previously, and it has been suggested that the adsorption of Co by Mn oxides is formed by oxidation of Co^{2+} to Co^{3+} followed by lattice replacement of Mn^{3+} by Co^{3+} (Sager, 1992; Jones and Jarvis, 1981).

A drop in the exchangeable fraction, F1, is also observed, and may be explained by conversion to the fraction associated with Mn oxides, F3. A slight increase in the oxidizable fraction, F5, is also observed. The major speciation change below 1 m is the conversion of the fraction associated with Mn oxides, F3, and oxidizable fraction, F5, to the residual fraction, F6.

Manganese

The easily reducible, or fraction associated with Mn oxides, is the highest in the surface layers of the old slime dam. This is followed by the oxidizable fraction, then the acid soluble, and the exchangeable fraction. The residual fraction is the lowest at 6%. From Figure 5 the behaviour of Mn appears to be characterised by the conversion of the easily reducible, oxidizable, acid soluble and exchangeable fractions to the reducible (F4) and residual (F6) fractions in the surface layers. With depth the reducible fraction F4 is further converted to the Mn oxides, with the consequent increase in the residual fraction, F6. The increase in the residual fraction, F6, for manganese is due to precipitation of hydrous Mn oxides.

Other elements which show an increase in the residual fraction are Cr, Zn, Co and Ni. Table 4 shows Pearson's correlation factors (Minitab, 1994) for the residual fractions for the elements studied (except Cd). The high positive correlation factors for Cu, Co, Zn and Cr with the residual fraction of Mn, all greater than 0.9, suggest that the increase in the residual fraction for these elements is due to co-precipitation with Mn oxides. Co-precipitation of Ni and Zn in Mn oxides was reported previously (Jones and Jarvis, 1981), while uptake of Pb, Cu and Cd by freshly prepared hydrous Mn(IV) oxide, from acetate buffer, was reported to be nearly complete over the pH range 3 to 9 (Sager, 1992; Aualiitia and Pickering, 1987). It is interesting to note from Table 4 that Ni, Cu, Co, Zn, Cr, and Mn all show negative correlation factors with the residual fraction of iron, Fe(F6), showing that these

elements do not co-precipitate with hydrous Fe(III) oxide under the conditions prevailing in the slime dams.

Chromium

Figure 2 shows that the oxidizable fraction F5 is the highest fraction in the surface layers of the slime dam. From Figure 5 the behaviour of Cr in the slime dam is characterised by the oxidation of this fraction to the reducible fraction F4. Below the 1 m level, both the F4 and F5 fractions are converted to the residual fraction, F6. The concentration of Cr^{3+} in well aerated soils is controlled by the formation of chromic oxides or hydroxides which are stable and of very low solubility (Jones and Jarvis, 1981).

Copper

From Figure 5, the major speciation change for Cu in the surface layers with time appears to be conversion of the reducible fraction, F4, to the oxidizable fraction, F5, and the acid soluble fraction, F3. Below 1 m, the acid soluble fraction is also converted to the oxidizable fraction, F5. The net result is a continuous increase in the oxidizable fraction, F5, with depth. Cu is unique in this respect. Cu^{2+} is known to form very stable complexes with organic matter over a wide range of pH (Sager, 1992; Jones and Jarvis, 1981). It was pointed out above that Cu forms a complex anion with the CN^- ion. The complex ion, $\text{Cu}(\text{CN})_2^-$, has a spiral polymeric structure in which each Cu(I) atom is bound to two CN-carbon atoms, and one CN-nitrogen atom in a nearly coplanar array (Cotton and Wilkinson, 1972b). The increase in F5 for Cu can only be explained by assuming that this polymeric ion is very stable, and is formed as the CN^- ion is released by the decomposition of the cyanide complexes of the other metals under the increasing acidic conditions.

Some conversion of the acid soluble fraction to the residual fraction also occurs, probably as a result of co-precipitation with Mn oxides. Co-precipitation of Cu in Fe and Mn oxides has been reported (Sager, 1992; Jones and Jarvis, 1981).

Zinc

Figure 2 shows that the oxidizable fraction, F5, is the highest in the surface layer of the old slime dam. This is followed by the exchangeable fraction, F1, then the reducible fraction, F4. The acid soluble (F2), easily reducible (F3) and residual (F6) fractions are very low in the surface layer. From Figure 5 the major speciation change in going from the surface to 1 m depth is the conversion of the exchangeable fraction, F1, and

reducible fraction, F4, to the acid soluble (F2) and easily reducible or fraction associated with Mn oxides (F3). Zinc carbonates and hydroxo carbonates are known (Cotton and Wilkinson, 1972c).

The major speciation change for Zn below the 1 m level is the conversion of the acid soluble (F2), the easily reducible (F3), the reducible (F4) and the oxidizable (F5) fractions to the exchangeable fraction (F1), and residual fraction (F6). The conversion to free Zn^{2+} ions results from the reduced pH at the base of the slime dam, while the increase in the residual fraction arises from co-precipitation with Mn oxides as discussed under Mn.

Nickel

Figure 5 shows that the major speciation changes for Ni above the 1 m level involve the conversion of (a) the acid soluble fraction, F2, to the exchangeable fraction F1 probably as a result of the dropping pH, and (b) conversion of the fraction associated with hydrous Fe oxides, F4, to the residual fraction F6, via co-precipitation with Mn oxides. Below the 1 m level, we see the conversion of the acid soluble fraction (F2), the fraction associated with hydrous Mn oxides (F3), the fraction associated with hydrous Fe oxides (F4), and oxidizable fraction (F5) to the residual fraction (F6) via co-precipitation with Mn oxides as discussed above.

Mobilities of the elements

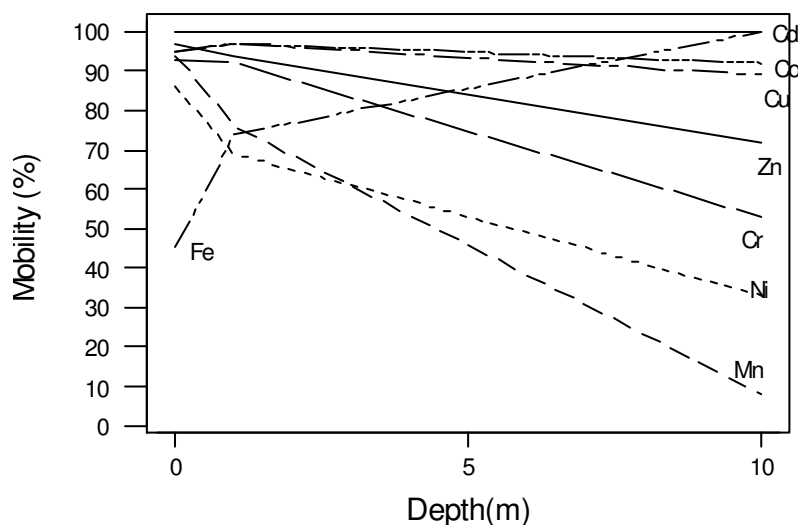
Table 5 shows the overall mobilities of the elements in the two slime dams. Cd is 100% mobile in both slime dams. The order of mobilities in the surface layers of the current slime dam for the rest of elements studied increases as follows: $\text{Fe} = \text{Ni} < \text{Cr} < \text{Cu} < \text{Mn} < \text{Co} < \text{Zn}$. Fe and Ni have the lowest mobilities at 54%, while Zn has the highest at 83%.

Figure 6 shows the profiles of mobilities of the elements as a function of depth in the old slime dam. Cd is again 100% mobile throughout the slime dam. In general, mobilities are very high, >90%, in the surface layers of the slime dam for all the elements studied with the exception of Fe. For Fe, mobility increases with depth, which is evidence of acid mine drainage.

At the 1 m level the order of mobilities is $\text{Ni} < \text{Fe} < \text{Mn} < \text{Cr} < \text{Zn} < \text{Cu} = \text{Co} < \text{Cd}$. This order is maintained at the base of the slime dam, that is, 10 m level, except that (a) the order for Mn and Ni is reversed, and (b) mobilities drop further. Mobility at 10 m increases in the order $\text{Mn} < \text{Ni} < \text{Cr} < \text{Zn} < \text{Cu} < \text{Fe} = \text{Cd}$. Cadmium and Fe show unique mobility patterns, while the rest of the elements studied show a definite pattern of high mobilities in the surface layers which decreases with depth. The decrease in mobilities follows the order $\text{Mn} > \text{Ni} > \text{Cr} > \text{Zn} > \text{Cu} > \text{Co}$. This trend is attributed to co-precipitation with Mn

Table 5. Mobility of the elements in the current slime dam (CSD) and old slime dam (OSD).

Element	CSD: Surface	OSD: Surface	OSD:1 m	OSD:10 m
Cd	100	100	100	100
Mn	73	94	76	8
Ni	54	86	69	33
cu	68	95	97	89
Fe	54	45	74	100
Co	80	95	97	92
Cr	60	93	92	53
Zn	83	97	94	72

**Figure 6.** Potential mobility as a function of depth in the old slime dam.

oxides. Table 6 shows ionic radii for the metals studied (Evan, 1992), while Figure 7 shows a regression plot of percentage residual fraction, F6, for the elements as a function of ionic radii. It is apparent from Table 6 and Figure 7 that co-precipitation of the metals by Mn oxides or CaCO_3 is related to the size of the ion. Thus because of its large size, Cd(II) does not co-precipitate with Mn oxides, but co-precipitates with CaCO_3 . On the other hand Fe does not co-precipitate with Mn because of its small size, while for Ni, Cr, Co, Cu and Zn co-precipitation with Mn decreases with increase in the size of the ion.

This trend suggests a tunnel or porous structure for the precipitated Mn oxides, such that the large Cd ion cannot enter the pores and therefore does not co-precipitate with the Mn oxides, while the small Fe(III) co-ordination 4 ion moves freely through the pores and is not retained. For Ni, Cr, Co, Cu and Zn the extent of co-precipitation decreases with increase in the size of the ion. Various forms of hydrous Mn(IV) oxides with tunnel structures have been reported (Burns and Burns, 1980;

Clearfield, 1988; Tsuji and Abe, 1984; Tsuji et al., 1992; Tsuji and Komameni, 1993; Tsuji et al., 1993). Figures 2 and 5 show that Fe exists mainly as the carbonate (F2) and the exchangeable fraction (F1) at the base of the slime dam. The low pH at the base of the slime dam results from the oxidation of sulphides; hence the major ligand in the exchangeable fraction must be the sulphate ion. Considering the large size of Ni(II) (0.69 Å), the high extent to which Ni co-precipitates with Mn oxides in Figure 7 suggests oxidation of Ni(II) to Ni(III) before co-precipitation as has been suggested by Sager (1992) and by Jones and Jarvis (1981).

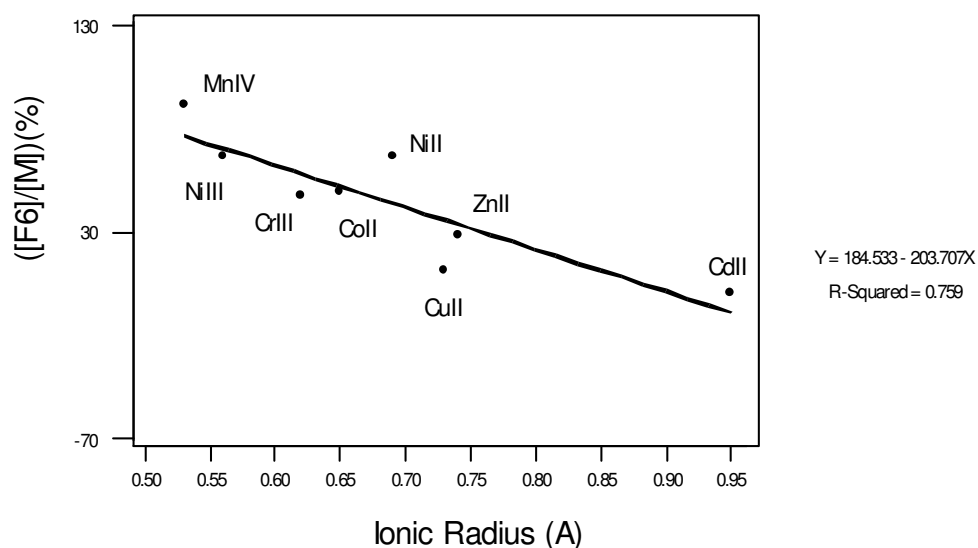
Conclusions

From the foregoing discussion we conclude that speciation of Cd, Mn, Ni, Cr, Cu, Co and Zn within the slime dams depends on the stability of the metal cyanide complexes formed during the cyanidation process, and on the ease with which the metals co-precipitate with Mn

Table 6. Ionic radii (R_i) of the elements studied.

Ion	Coordination number	$R_i(\text{\AA})$
Cd(+2)	4	0.78
	8	0.95
	8	1.10
Ca(+2)	6	1.00
	8	1.12
Cd(+2)	6	0.95
Co(+2)	6	0.65
Co(+3)	6	0.55
Cu(+2)	6	0.73
Zn(+2)	6	0.74
Cr(+3)	6	0.62
Ni(+2)	6	0.69
Ni(+3)	6	0.56
Mn(+4)	6	0.53
Fe(+3)	6	0.55
Fe(+3)	4	0.49

Source: Evan Jr. (1992).

**Figure 7.** Percentage residual fraction (F6) at the base of the old slime dam as a function of ionic radius (co-ordination number (CN) 6): [F] = concentration of speciation fraction; [M] = total element concentration.oxides and/or CaCO_3 .

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