

Investigation of the immobilisation/mobilisation of nickel, copper, chromium and zinc following co-disposal of activated sewage sludge with synthetic refuse

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Abstract

Laboratory microcosms were packed with synthetic refuse and waste activated sewage sludge in two ratios (4.1:1 and 4.1:2 v/v). The sludge was spiked (100 mg·ℓ⁻¹ or 200 mg·ℓ⁻¹) with the salts of each of four heavy metals (Ni²⁺, Cu²⁺, Cr³⁺ and Zn²⁺). Subsequently, the metal concentrations were increased progressively. For all the microcosms, including an unperturbed control, unbalanced fermentations resulted as evidenced by low pH values. Thus, heavy metal presence was not the sole cause. The leached metal concentrations were in a consistent order with high Zn and Ni concentrations recorded compared with immobilised Cr and Cu. After 15 weeks of operation, despite extensive retention, increases in Cr, Ni and Zn were detected in the leachates following elevated loadings. Due to the high redox potentials (+2 to +170 mV), precipitation of the metals as insoluble sulphides was not attainable.

Introduction

Heavy metals are present in a range of industrial wastes together with industrial and household products. They are, therefore, components of household refuse (Knox, 1989). Since there is a wide variety in the chemical and environmental behaviour of heavy metals (Knox, 1989), their fates in co-disposal landfills are of concern (Gregson et al., 1988).

In co-disposal landfills, potential heavy metal toxicities to micro-organisms may be maximised or minimised depending on the metal-binding capacity of a particular sludge (MacNicol and Beckett, 1989), the ion and organic constituent interactions (Babich and Stotzky, 1985; Fletcher and Beckett, 1987) and the specific dissolved metal species present and their concentrations (Mueller and Steiner, 1992).

This picture can be complicated further by the application of covering soil between the refuse cells and, more particularly, by the activity of microbial catabolic species. Clayey impermeable material, for example, is dominated by fermentative populations while respiratory microbial species attach to the more sandy soils (Chapelle, 1993). The former species catabolise complex organic molecules and release intermediates which, in turn, are oxidised by respiratory species by reducing available electron acceptors (oxygen, nitrate, manganese hydroxides, iron hydroxides, sulphate and carbon dioxide). As a consequence, redox gradients are generated. Heavy metal precipitations as sulphides are related indirectly to redox potential. Such precipitations play a key role in the immobilisation of heavy metals in the refuse mass.

For this investigation of immobilisation/mobilisation of heavy metals following co-disposal operation, four species (Ni²⁺, Cu²⁺,

Cr³⁺ and Zn²⁺) were chosen on the basis of their variable mobilities and presence in refuse and sewage sludge.

Materials and methods

Refuse

A synthetic refuse was prepared by combining equal volumes of shredded paper from a paper recycling plant and vegetable plus garden wastes. The moisture content of the refuse was determined by taking two samples (100 g each) and drying at 60°C for 72 h. The samples were weighed before and after drying and the moisture content was determined by the mass difference.

Sewage sludge

Activated sewage sludge was collected from the return channel of Darvill Sewage Works, Pietermaritzburg. The moisture content was determined as above after drying at 70°C.

Microcosm construction and operation of microcosms

Six glass columns (length 50 cm, i.d. 5.3 cm) were used (Percival and Senior, 1998). The microcosms were packed with synthetic refuse ± sewage sludge (Table 1). Two refuse:sewage sludge packing ratios of, 4.1:1 and 4.1:2 (v/v) were used (Percival, 1996), while the refuse-packing density was ~830 kg·m⁻³.

Glass wool was placed at the base of each column to prevent refuse/sludge displacement. The columns were incubated in the dark at 30°C in a temperature-controlled box fitted with heating elements. Fermentation gases were vented from the microcosms via Zn acetate (0.1% m/v) gas traps to collect hydrogen sulphide as insoluble zinc sulphide. Leachate was recycled daily by removing 40 ml from the base of each microcosm with a hypodermic needle connected to a plastic syringe (20 ℓ) and reintroducing it to the top of the column.

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Microcosm	Packing materials	Heavy metal loading
1	Refuse + sludge (4.1:1)	Heavy metal spiked sludge (100 mg·t ⁻¹)
2	Refuse + sludge (4.1:1)	Sludge not spiked
3	Refuse + sludge (4.1:2)	Heavy metal spiked sludge (200 mg·t ⁻¹)
4	Refuse + sludge (4.1:2)	Sludge not spiked
5	Refuse	dH ₂ O plus heavy metal (200 mg·t ⁻¹)
6	Refuse	dH ₂ O

Microcosms 3 and 5, week 13; 400 mg·t⁻¹, Microcosm 1 and 800 mg·t⁻¹, Microcosms 3 and 5, week 14; and 800 mg·t⁻¹, Microcosm 1 and 1 600 mg·t⁻¹, Microcosms 3 and 5, week 15. The unspiked microcosms received equivalent volumes of dH₂O at each dosage point.

Analyses

pH

A Crison MicropH 2002 meter fitted with a pH electrode (Ingold) was used to determine the supernatant pH values.

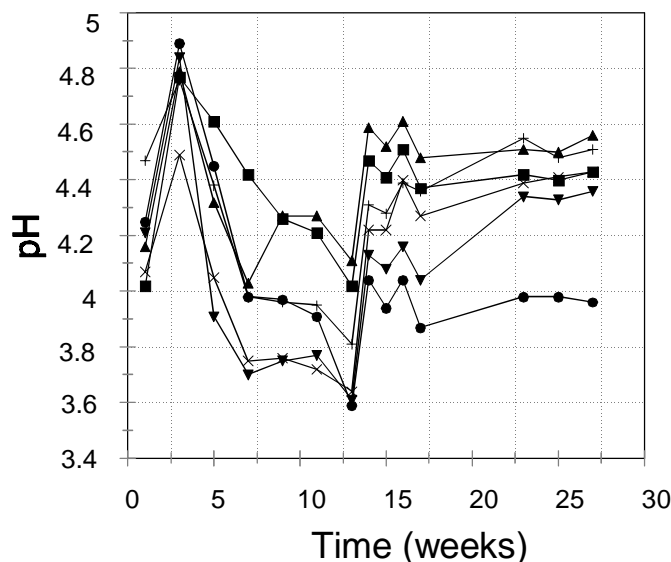


Figure 1

Changes in leachate pH of Microcosm 1 (+), 2 (▼), 3 (■), 4 (X), 5 (▲) and 6 (●) packed as detailed in Table 1

Heavy metals

The activated sewage sludge was spiked with heavy metal salts prior to packing. One hundred mg·t⁻¹ (refuse : sludge ratio 4.1:1) and 200 mg·t⁻¹ (refuse : sludge ratio 4.1:2) each of nickel (Ni²⁺) sulphate, zinc (Zn²⁺) sulphate, cupric (Cu²⁺) chloride and chromium (Cr³⁺) chloride were dissolved in the sludge supernatant.

Refuse control microcosms

For Microcosm 5, 200 mg·t⁻¹ of each of the four heavy metal salts was dissolved in distilled water (dH₂O) prior to addition while dH₂O alone was added to Microcosm 6.

Increases in heavy metal loadings

The loadings of Microcosms 1,3 and 5 were increased from week 11 by applying heavy metal salt solutions (30 mL, 4.1:1; 60 mL, 4.1:2) at an irrigation rate of 10 mL·h⁻¹ at each dosage point by means of plastic syringes (20 mL) fitted with hypodermic needles.

The concentrations added to each of the microcosms for each metal were as follows: 150 mg·t⁻¹, Microcosm 1 and 300 mg·t⁻¹, Microcosms 3 and 5, week 11; 200 mg·t⁻¹, Microcosm 1 and 400 mg·t⁻¹,

Redox potential

The redox potential of leachate samples was determined with a combined platinum redox electrode (Crison) connected to a Crison MicropH 2002 meter. A ferrous/ferric solution was used to standardise the redox electrode before and after analysis. The standard solution contained (g·t⁻¹ dH₂O): ferrous ammonium sulphate, 39.21; ferric ammonium sulphate, 48.22; and concentrated sulphuric acid, 56.2 L. The redox reading of this solution averaged +468 mV.

Heavy metals

A Varian Spectra AA-200 atomic absorption spectrophotometer (AAS) with a nitrous oxide-acetylene flame, to minimise chemical interferences, was used. The conditions for each metal analysis were as follows: Cr³⁺: wavelength, 357.9 nm; spectral band pass, 0.2 nm; lamp current, 7 mA; Cu²⁺: wavelength, 324.7 nm; spectral band pass, 0.5 nm; lamp current, 4 mA; Ni²⁺: wavelength, 232.9 nm; spectral band pass, 0.2 nm; lamp current, 4 mA; and Zn²⁺: wavelength, 213.9 nm; spectral band pass, 0.1 nm; lamp current, 5 mA. Prior to analysis, each supernatant sample was filtered through an 0.45 µm cellulose acetate membrane filter.

To determine the initial concentrations of Cr, Cu, Ni and Zn, refuse and sewage sludge (supernatant and solids) samples were centrifuged in a Beckman J2 HS Centrifuge at 10 000 r·min⁻¹ x g for 25 min. Thereafter, the supernatants were analysed.

The residual solids were then oven-dried at 60 °C for 72 h. Approximately 1.0 g, to the nearest mg, of each of the dried samples was transferred into a wide-form porcelain crucible. After ashing in a pre-heated furnace at 500 °C for 2 h and cooling, the residuals were moistened with dH₂O and 10 mL of 4M HCl (32% v/v) / HNO₃ (70.5% v/v) acid mixture was added.

Digestion (at 163±5 °C) on a sand bath followed for 20 min. The preparations were then transferred quantitatively to 100 mL volumetric flasks with a glass rod to prevent losses and were diluted to volume with dH₂O. Filtration through 3.0 µm cellulose acetate membrane filters followed. Thereafter, the crucibles and the precipitates on the filters were washed with dH₂O. The digested sample supernatants were then analysed by AAS.

Results

The moisture content of the refuse and sewage sludge was 45.5% (m/m) and 89% (m/m), respectively.

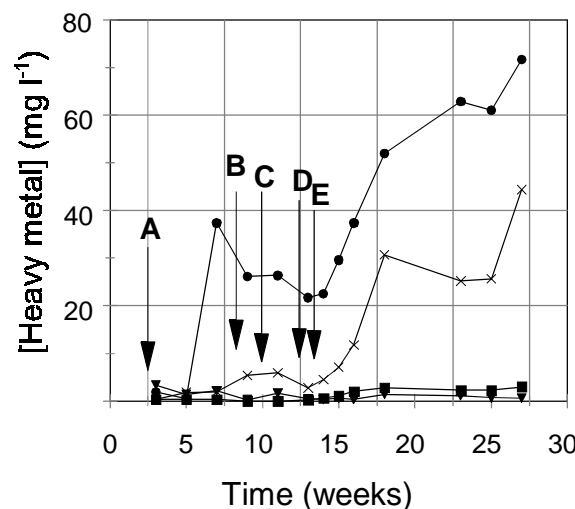
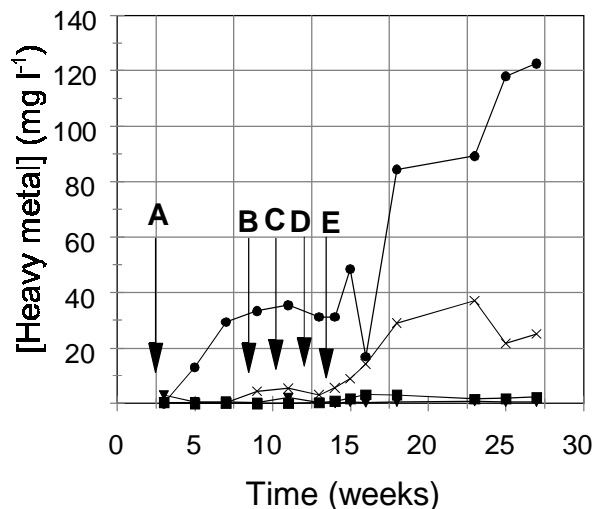
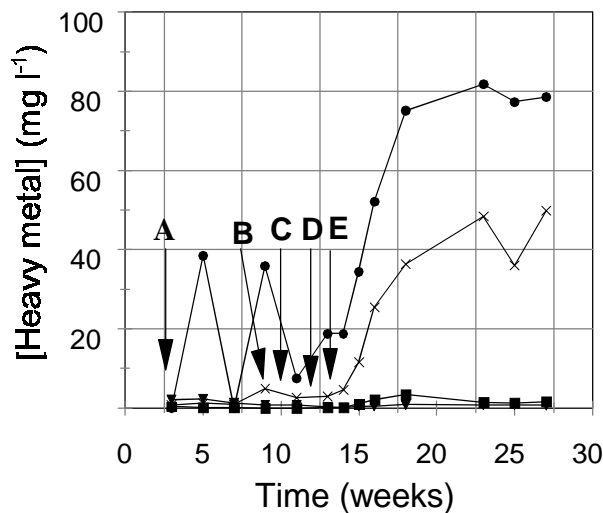


Figure 2
Changes in leachate Cr (■), Cu (▼), Ni (X) and Zn (●) concentrations of Microcosm 5 (a), 1 (b) and 3 (c) following metal supplementations of 100 mg·l⁻¹ (A), 150 mg·l⁻¹ (B), 200 mg·l⁻¹ (C), 400 mg·l⁻¹ (D) and 800 mg·l⁻¹ (E) for Microcosm 1 and 100 mg·l⁻¹ (A), 300 mg·l⁻¹ (B), 400 mg·l⁻¹ (C), 800 mg·l⁻¹ (D) and 1 600 mg·l⁻¹ (E) for Microcosms 3 and 5

pH

Low pH values (≤ 4.9) (Fig. 1) were recorded during the 27-week study period. The synthetic refuse used facilitated the production of volatile fatty acids (VFA) in the solid-state fermentations (Barlaz et al., 1989) which, in turn, affected the pH. The presence of heavy metals did not facilitate the low pH values due to heavy metal toxicity and, specifically, the inactivation of hydrogen sinks as the unspiked columns (Microcosms 2,4 and 6) exhibited the same trends.

Redox potential (E)

The redox potentials recorded did not approach the optimum for the solid-state refuse methanogenic fermentation and were in the range of +2 to +170 mV (data not shown). The metal-spiked and non-spiked microcosms recorded comparable leachate redox potentials.

The precipitation of metal species relies on the aqueous biodegradation of refuse. Newton (1977), Pohland and Gould (1980) and Pohland et al. (1982) concluded that sulphide precipitation may be the ultimate control for many heavy metals in refuse. In the present study, sulphide precipitation probably did not contribute to metal immobilisation as the high E values recorded excluded sulphate reduction which is operated at E values of ± 220 mV (Atlas, 1984). Also, the low pH values (Fig.1) obviated other precipitations since an alkaline pH is required to facilitate hydroxide, oxide and carbonate precipitation (Gadd, 1986).

Heavy metal mobility and immobilisation

Refuse microcosms

Microcosms 5 and 6 leached Ni masses (Figs. 2a and 3a) of 2.71 mg and 0.43 mg of their totals of 271.95 mg and 21.95 mg, respectively (Table 2). For Microcosm 5, an increase was observed following the second supplementation, but a marked increase was particularly evident after it received the 5th metal loading at week 15 (Fig. 2a). Although this microcosm received a total loading of 250 mg, > 99 % immobilised compared to ~98.04 % in Microcosm 6. The Ni holding capacity of the refuse was not exceeded by the loading increases.

Higher Cu concentrations were measured in the leachate of Microcosm 5 (total mass leached 0.15 mg, ~0.06 %) than Microcosm 6 (0.06 mg, ~1.01 %). Following each of the first four Cu loadings, progressive leachate concentration reductions resulted, probably due to adsorption. The total leachate masses of Cr were comparable for the two microcosms (0.15 mg, ~0.05 % and 0.17 mg, ~0.68 % for Microcosms 5 and 6, respectively) (Figs. 2a and 3a). For both metals equal masses (0.15 mg) were displaced from Microcosm 5, although the total loading of Cr (274.85 mg) was higher than the equivalent (255.93 mg) for Cu (Table 2).

The total Zn leached in the 27 weeks of operation of Microcosm 6 was 17.55 mg while the initial mass in the refuse was 64.98 mg. In contrast, for Microcosm 5, 6.23 mg were leached from a total loading of 314.98 mg. The mass of the metal leached from the

	Chromium	Copper	Nickel	Zinc
Initial mass				
Synthetic refuse:				
Supernatant	0	2.45	4.95	12.23
Solid	24.85	3.49	17.0	52.75
Total:	24.85	5.94	21.95	64.98
Sewage sludge:				
Supernatant	0.003	0.02	0.013	0.01
Solid	26.63	20.06	18.31	373.65
Total:	26.63	20.08	18.32	373.66
Total (refuse plus sludge):	51.48	26.02	40.27	438.64
Heavy metal loadings:				
Microcosm 1 (4.1:1)	65.7	65.7	65.7	65.7
Microcosms 3,5 (4.1:2)	250	250	250	250
Microcosm 1				
Total initial mass	51.48	26.02	40.27	438.64
Heavy metal loading	65.7	65.7	65.7	65.7
Mass leached	0.2	0.13	1.88	7.85
% not immobilised	~0.17	~0.14	~1.77	~1.56
Microcosm 2				
Total initial mass	51.48	26.02	40.27	438.64
Mass leached	0.08	0.06	0.21	1.5
% not immobilised	~0.16	~0.23	~0.52	~0.34
Microcosm 3				
Total initial mass	51.48	26.02	40.27	438.64
Heavy metal loading	250	250	250	250
Mass leached	0.81	0.17	2.01	5.41
% not immobilised	~0.27	~0.06	~0.69	~0.79
Microcosm 4				
Total initial mass	51.48	26.02	40.27	438.64
Mass leached	0.07	0.08	0.19	1.46
% not immobilised	~0.14	~0.31	~0.47	~0.33
Microcosm 5 (Control)				
Total initial mass (refuse)	24.85	5.93	21.95	64.98
Heavy metal loading	250	250	250	250
Mass leached	0.15	0.15	2.71	6.23
% not immobilised	~0.05	~0.06	~0.99	~1.98
Microcosm 6 (Control)				
Total initial mass (refuse)	24.85	5.93	21.95	64.98
Mass leached	0.17	0.06	0.43	17.55
% not immobilised	~0.68	~1.01	~1.96	~27

loaded microcosm was lower than that of the control microcosm as was also apparent for Cr (Table 2).

Co-disposal microcosms

Leached Ni progressively increased in both the metal-dosed microcosms (Microcosms 1 and 3) (Figs. 2b,c) and similar increases were recorded in the unspiked microcosms (Microcosms 2 and 4) (Figs. 3b, c). The leached masses were 1.88 mg, 2.01 mg, 0.21 mg and 0.19 mg of their total masses of 105.97 mg, 290.27 mg, 40.27 mg and 40.27 mg, respectively (Table 2). Microcosm 1 received a total spiking of 65.7 mg and ~98.23% immobilised compared to Microcosm 3 which received 250 mg with > 99% immobilised. Elevated Cr, Ni and Zn concentrations were measured in the leachates of the metal-dosed microcosms (Microcosms 1 and 3) (Figs. 2b, c) after week 15 while similar increases were detected in the unspiked microcosms (Microcosms 2 and 4) (Figs. 3b, c).

For Cu, the total displaced never exceeded 0.17 mg (Microcosm 3) of the total mass (91.72 mg, Microcosm 1; 276.02 mg, Microcosm 3; and 26.02 mg, Microcosms 2 and 4). Thus, it appeared that the Cu-holding capacity was not exceeded. Cr showed similar trends. In the metal-dosed microcosms, ~0.17% and ~0.27% remained in solution in Microcosms 1 and 3 (Figs. 2b, c), respectively. In the unspiked microcosms (Microcosms 2 and 4) (Figs. 3b,c) ~0.16% and ~0.14% were not immobilised. The total displaced Cr of Microcosm 3 was 0.81 mg of the total mass (301.48 mg).

Zn showed distinct displacement increases with recorded leachate concentrations $\geq 118 \text{ mg}\cdot\text{L}^{-1}$ (Weeks 25 - 27) and $> 60 \text{ mg}\cdot\text{L}^{-1}$ (Weeks 23 - 27) for Microcosms 1 and 3, respectively (Figs. 2b,c). Higher total masses were recorded in the leachates of Microcosms 1 and 3 (7.85 mg, ~1.56% and 5.41 mg, ~5.4% of 504.34 mg and 688.64 mg, respectively) compared with Microcosms 2 and 4 (1.5 mg, ~0.34% and 1.64 mg, ~0.33% of 438.64 mg, respectively).

The possibility existed that the prolonged acidic conditions favoured free cations since it has been reported that an acid pH and high E facilitate increased metal solubility (Wood and Wang, 1983). Since metal adsorption is usually enhanced at neutral pH (Ferris et al., 1989), the low pH trends recorded (Fig. 1) did not favour immobilisation. Despite this, the masses of Cr, Cu, Ni and Zn displaced from Microcosm 3 were low compared with the original loadings (Table 2).

Refuse vs co-disposal microcosms

Comparing the heavy metal concentrations of the leachate of Microcosms 5 and 6 (Figs. 2a and 3a) and the co-disposal columns (Microcosms 1 to 4)

(Figs. 2b,c and 3b,c), no distinct differences were detected in the metal-dosed microcosms for Cr and Cu. For each, an initial Cu peak was followed by a progressive decrease despite the increased loadings. When the percentages of Cu leached from the microcosms are taken into account (~0.14%, Microcosm 1; ~0.06%, Microcosm 3; ~0.06%, Microcosm 5) (Table 2) it is apparent that the refuse/sludge Cu binding capacity was not exceeded. Ni exhibited higher mobility than Cu and Cr (~1.77%, Microcosm 1; ~0.69%, Microcosm 3; ~0.99%, Microcosm 5).

The unspiked refuse microcosm (Microcosm 6) (Fig. 3a) and unspiked co-disposal microcosms (Microcosms 2 and 4) (Figs. 3b,c) recorded variable masses of displaced Cr, Cu and Ni and these variabilities were even more pronounced for Zn. It should be noted, however, that although the masses of Zn displaced were high, the immobilised masses were also high. This was particularly evident in Microcosm 6 where ~73% immobilised while 17.55 mg of the total mass of 64.98 mg leached.

Comparing the Zn concentrations in the leachates of Microcosms 1, 3 and 5 (Figs. 2 a,b,c) similar trends were observed (~98.44%, ~99.21% and ~98.02% immobilised while 7.85 mg, 5.41 mg and 6.23 mg of the total masses of 504.34 mg, 688.64 mg and 314.98 mg leached) (Table 2).

As sewage sludge was excluded from the controls, the cation-exchange capacity (MacNicol and Beckett, 1989) was probably reduced. In this study the presence of sludge appeared to have a minimal effect on heavy metal retention compared with the refuse microcosms.

Discussion

Factors such as the leachate pH and redox potential, waste type and age, waste surface properties and the effects of changing surface properties during fermentation are responsible for heavy metal immobilisation, mobilisation and precipitation as insoluble sulphides in co-disposal landfill sites. In this investigation, unbalanced fermentations developed with acidogenesis > acidotrophy (Ehlers et al., 1999). It was very difficult to identify any possible bactericidal/bacteriostatic effects of the added metals.

When the metals were added via sewage sludge or in solution, extensive retention occurred, even at low pH values. For Ni and Zn, elevated leachate concentrations were still accompanied by extensive retention. Metal displacements via leachate showed relatively consistent patterns which could be attributed possibly to the metal-holding capacity of the refuse and/or sewage sludge for a specific metal, i.e. the cation exchange preference for one metal species compared with another.

As the behaviour of any one metal may be changed by its chemical and biological environment, a strict ranking would be unjustified on the basis of the data available, but the general order of retention appeared to be: Cr>Cu>Ni≈Zn.

Dual co-disposal of activated sewage sludge plus heavy metal-containing wastewaters with refuse could be advantageous since studies with sludges have shown little enhancement of leachate metal concentrations (Knox, 1989). Sewage sludge co-disposal *per se* could be advantageous if the heavy metal adsorption capacity of the refuse is exceeded as the solid-state fermentation progresses. It could also be disadvantageous, however, if the elevated adsorbed concentrations are displaced in response to acidogenesis.

Thus, one important aspect of heavy metal co-disposal that is the focus of an ongoing investigation is the status of the solid-state fermentation and the effect that it has on metal retention and mobilisation. The onset and progress of the fermentation should affect metal mobilisation as waste surface characteristics and the

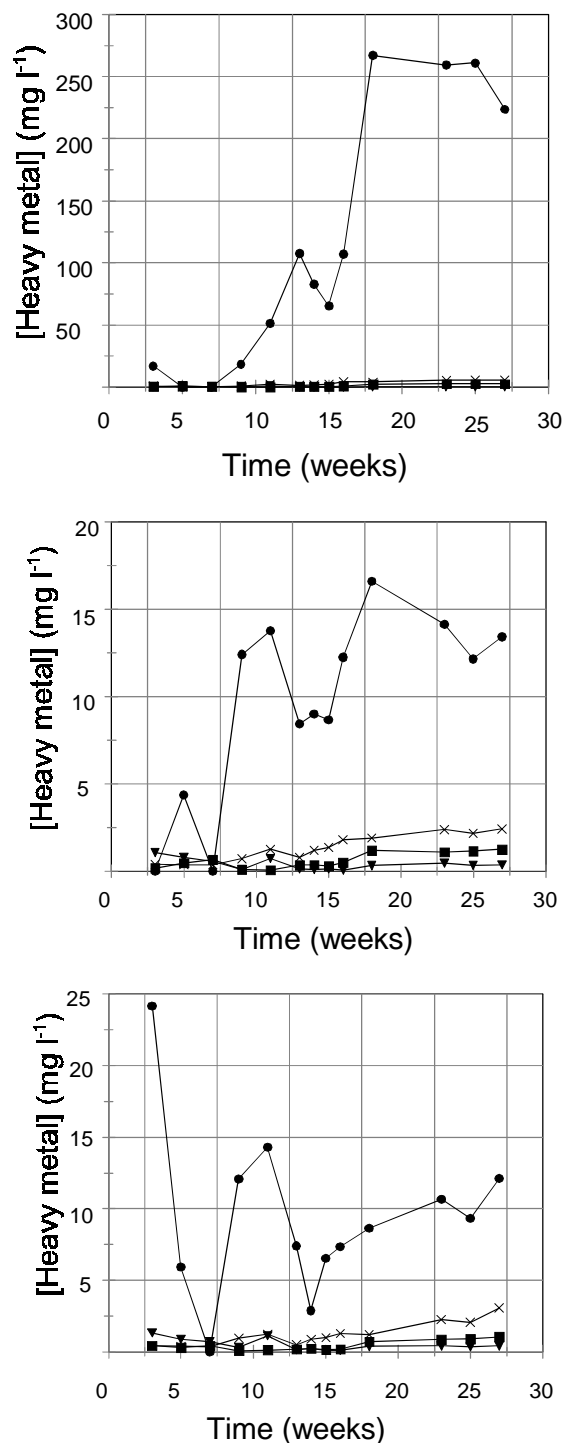


Figure 3
Changes in leachate Cr (■), Cu (▼), Ni (X) and Zn (●) concentrations of Microcosm 6 (a), 2 (b) and 4 (c)

changes of surface properties should contribute to metal displacement.

Acknowledgements

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