The retention capabilities of soils at Batang Berjuntai and Ampar Tenang as natural clay liners for landfill systems using leaching column test and selective sequential extraction analysis

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Abstract: Clay liners have the ability to interact chemically with leachate. If suitable clay liner can be identified, it can help to attenuate the migration of leachate to groundwater and surface water. In this study, leaching column tests were used to determine the retention capability of heavy metals for two types of soils collected adjacent to a landfill in Selangor. The active landfill sites chosen are Kg. Hang Tuah in Batang Berjuntai (HMS) and Ampar Tenang, Sepang (ARA) where the HMS samples are metasediment soil and ARA samples are river alluvium soil. Selective sequential extraction (SSE) was used to study the retention mechanisms of heavy metals in the soil columns obtained from leaching column test experiments. Acid digestion was later used to check the validity of the SSE results. Breakthrough curves for metasediment soil from Kg. Hang Tuah show good retention of heavy metal ions with relative concentration, C_e/C_o (10^{-1} - 10^{-5}) compared to river alluvium soil from Ampar Tenang with relative concentration, C_e/C_o (10^{-1} - 10^{-4}). This corresponds with the pH of the effluents and the pore fluid where the HMS samples are more alkali compared to ARA samples. Generally, HMS and ARA samples have same ranked order of buffering capacity; Cu>Zn>Pb>Ni. The distribution of the heavy metals with soil constituents are ranked in the following phases: Exchangeable > Carbonates > Hydroxides > Residuals > Organics

Abstrak: Pelapik lempung mempunyai keupayaan untuk bertindak secara kimia terhadap cecair larut lesap. Sekiranya pelapik lempung yang sesuai dapat dikenalpasti, ia dapat membantu bagi mengurangkan migrasi cecair larut lesap ke dalam air bawah tanah dan air permukaan.Dalam kajian ini, ujian kolum turasan telah digunakan untuk mengenalpasti keupayaan menahan logam-logam berat bagi dua jenis tanah yang telah diambil berdekatan tapak pelupusan sisa di Selangor. Tapak pelupusan sisa pepajal yang aktif yang dipilih ialah di Kg. Hang Tuah di Batang Berjuntai (HMS) dan di Ampar Tenang, Sepang (ARA) di mana sampel HMS merupakan tanah metasedimen dan ARA pula merupakan tanah aluvium sungai. Rangkaian pengestrakan terpilih (SSE) telah digunakan untuk mengkaji mekanisma menahan logam-logam berat di dalam kolum tanah yang diperolehi daripada eksperimen ujian kolum turasan. Pencemaran asid telah digunakan untuk memastikan kesahihan keputusan SSE. Pecahan lengkung-lengkung bagi tanah metasedimen dari Kg. Hang Tuah menunjukkan penahanan ion logam berat yang baik dengan konsentrasi relatif, C_e/C_o (10^{-1}-10^{-5}) berbanding tanah aluvium sungai dari Ampar Tenang dengan konsentrasi relatif, C_e/C_o (10^{-1}-10^{-4}). Ini selari dengan nilai pH efluen dan cecair liang yang menunjukkan sampel HMS lebih beralkali berbanding sampel ARA. Keseluruhannya, sampel HMS dan ARA mempunyai kedudukan susunan kapasiti menampan yang sama; Cu>Zn>Pb>Ni. Taburan logam-logam berat dengan juzuk tanah telah disusun seperti fasa berikut: Tukarganti > Karbonat > Hidroksida > Residual > Organik

INTRODUCTION

Landfills are a significant source of groundwater contamination. One of the major problems with the management of waste dumps is the collection and treatment of leachate generated. The problem encountered when seeking suitable locations for landfill sites often include public concerns over the potential health and environmental impacts (Nunan, 1996). Leachate permeates into ground and surface waters, causing pollution and hence, it poses considerable hazards to the natural environment. Also, polluted groundwater is difficult to clean, and the cost to control the polluted groundwater is huge.

Compacted clay liners are the most popular and cheapest option. For liner material, clay liners have the ability to interact chemically with the leachate. If suitable clay liner can be obtained, it can help to attenuate the migration of leachate to groundwater and surface water.

The main objective of this study is to investigate the suitability of two soils to be used as lining material using leaching properties of the soils.

MATERIALS AND METHODS

Physico-chemical tests

Soil samples were taken from adjacent to two active landfill sites in Selangor (Fig. 1). The samples were taken from shallow depths from the ground surface; they are generally of weathering grade VI (Residual Soils). The physical and chemical properties tested are: natural water content, specific gravity (relative density), grain size distribution, Atterberg limits, compaction characteristics, permeability, pH of soils, carbonate ontent, specific

Figure 1. The location of active landfill sites and sampling stations

surface area (SSA), cation exchange capacity (CEC) and organic content.

The test methods adopted according to the British Standards BS1377 (1975) and the Geotechnical Research Centre (GRC) Laboratory Manual (1985), McGill University, Montreal, Canada. Thus for each example, SSA was determined using ethylene glycol monoethyl ether based on the method by Carter et al. (1965), carbonate contents were determined using titration method suggested by Hesse (1972) and CEC was determined using the method from American Society for Testing and Materials, ASTM D4319-83 (1994) with ammonium acetate at pH 7.0.

Species and concentrations of all cations are determined from analyses with the Atomic Absorption Spectrometer (AAS). Due to the fine-grained nature of the soils, identification of the constituent minerals was performed by X-ray diffraction technique (XRD) on a fully automated Siemens D-5000 Diffractometer.
Leaching column test

The leaching cell used consisted of a Plexiglas cylinder with diameter 100 mm and height 104 mm. The column soil samples were compacted at maximum dry density and optimum moisture content. There were two stages of leaching: a) saturation stage using distilled water and b) leaching stage using a test leachate. The leaching experiments were conducted under constant air pressure at 10 psi (68 kPa) to reduce the time factor for leachate transport through the soil columns.

The test leachate was obtained from Municipal Solid Waste Landfill and spiked with heavy metals; Pb, Cu, Zn and Ni. The pH of the test leachate was reduced to 1.45 to avoid metal precipitation at onset of leachate penetration into the soil, and also to promote increased mobility of the heavy metals in the soil columns. The concentration of Pb, Cu, Zn and Ni in the spiked leachate used in the column is presented in Table 1.

The effluents (leachate discharge) were collected and analysed at every 0.5 pore volume using AAS. At the end of the experiments the columns were extruded and the soil samples were sliced into six equal slices (~17 mm each). The soil slices were tested for exchangeable cations using ammonium acetate (pH 7.0), and pore water analysis was determined for their heavy metal content using the AAS.

Acid digestion

The intent of acid digestion analysis was to determine the total heavy metal in the soil after leaching test. The soil samples from leaching column tests, which were used for the SSE analysis, were sliced into six equal slices. About 200 mg of dry soil sample was placed into a clean dry savillex vial; Teflon container. The vial was placed in the fume cupboard before addition of 5 ml of

Table 1. Concentration of Pb, Cu, Zn and Ni in the spiked leachate (all ionic concentration in mg/l)

Composition	Concentration
pH	1.45
Conductivity, mS/cm	5.93
Pb	538.6
Cu	556.8
Zn	516.8
Ni	567.9

concentrated HF to the vial. It was then left overnight to digest on the hotplate. The solution obtained after digestion was reduced by partial evaporation, following which about 5 ml of aqua regia was add to the reduced solution. The sample was then digested for another 24 h and subsequently evaporated to obtain a dry sample. Following this, 5-6 ml of 5M HCl was added to the sample, which was left on a hotplate for several hours. The solution obtained from the digested soil slices was diluted with distilled water in a 100 ml plastic volumetric flask prior to analysis using the AAS.

Selective sequential extraction (SSE)

The intent of the SSE analysis was to determine the distribution of the partitioned heavy metals along the leaching column at the termination of 5 pore volume of leachate penetration. Methods of extraction have been adopted from Yong and Phadungchewit (1993), Yanful et al. (1988), Tessier et al. (1979) and Gupta and Chen (1975). The basic utility of SSE is its use of appropriate reagents to release different heavy metal fractions from soil solids by destroying the binding agents between the metal species to be detected (Yong and Phadungchewit, 1993).

The soil samples from leaching column tests, which were used for the SSE analysis, were sliced into six equal slices. For the SSE analysis, 1 g of the soil slice was weighed into the 50 ml polypropylene centrifuge tubes to avoid any loss of soil sediment during the extraction stages, only 1 g of soil was used in order to comply with the stage 5 requirement using HF.

The procedure for Pb, Cu, Zn and Ni extraction for the different sorption mechanisms were as follows:

Stage 1: Exchangeable cations- 8 ml of 1M Potassium Nitrate, KNO3. The pH was adjusted to the natural soil pH and shaken continuously for 1 hour. All metals retained released via cation exchange.

Stage 2: Carbonate- 8 ml of 1M Sodium Acetate (NaOAc) adjusted to pH 5.0 by acetic acid (HOAc) and agitated continuously for 5 hours to release metals which precipitated with carbonates.

Stage 3 :Oxides and hydroxides- 20 ml of 0.04M of Hydroxylamine hydrochloride (NH2OH.HCl) in 25% (v/v) Acetic Acid (HOAc), agitated occasionally at 96+3oC for 6 hours. This will extract all metals precipitated as hydroxides and/or adsorbed on the oxides or the amorphous hydroxides.

Stage 4 :Organics- Heavy metals bound to organic constituents in soil via complexation, adsorption and chelation. This extraction is devided into three phases- Phase i: 3 ml of 0.02M Nitric Acid (HNO3) and 5 ml of 30% H2O2 adjusted to pH 2.0 with HNO3 occasionally agitated for 2 hours at temperature 85+2oC. Phase ii- 3 ml of 30% H2O2 (at pH 2.0), intermittently agitated for 3 hours at temperature 85+2oC. Phase iii- 5 ml of 3.2M Ammonium Acetate (NH4OAc) in 20%(v/v) HNO3, diluted to 20 ml, and continuously agitated at room temperature for 30 minutes.

Stage 5: Residual Fractions- Metals that are bound to the soil solids via specific adsorption in soil mineral lattice will be extracted by digestion. The residue (after the previous 4 stages) was digested with 5 ml of hydrofluoric acid (HF), 5 ml of aqua regia i.e. nitric acid (HNO3) mixed with hydrochloric acid (HCl) and finally with 5 ml of hydrochloric acid (5M HCl).

In between the stages, solids-liquid separation was obtained by centrifuge. The supernatant collected and analysed, and the residue left was washed, centrifuged again, and the second supernatant discarded.

RESULTS AND DISCUSSIONS

Physico-chemical properties

Table 2 and Table 3 show the physical and chemical properties of soils. Specific gravity (Gs) for HMS soil samples are around 2.50 and ARA soil samples are around 2.34.

The particle size distribution for all soil samples are dominated by fine-grained components with silt sized particles more abundant than the clay-sized particle. The coarse fraction for all soil samples are less than 15%. However, the presence of lateritic bands or iron concretions in the residual soils increases the amounts of sand and gravel sized particles in the HMS soil samples. Generally, both of soils are grouped in good grade.

The plasticity for ARA soil samples are low compared to HMS soil samples. Liquid limits for HMS range from 30-60% and plasticity index values show a broad range from 14-35%.

The data plotted in Figure 2 shows that most samples have high clay activity. From the activity of clays, the clay minerals can be predicted. High activity of clays show the existence of montmorillonite mineral, moderate activity

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Table 2. Physical properties of soils.

Property	HMSs	ARAs
Gs, g/cm^3	2.44-2.63	2.22-2.42
Clay, %	20-30	10-27
Silt, %	45-56	42-71
Sand, %	11-15	2-45
Gravel, %	3-16	0
LL, %	38.5-57.0	38.9-50.0
PL, %	21.0-27.0	23.7-31.7
PI, %	14.2-35.0	11.3-25.3
W_{opt}, %	21-30	10-22
γ_{dmax}, g/cm^3	1.32-1.49	1.54-1.63
k, m/secs	2.38x10^{-8}	5.13x10^{-7}
Class	CH	ML

Gs = specific gravity; LL = liquid limit; PL = plastic limit; PI = plasticity index; W_{opt} = water optimum content; γ_{dmax} = maximum dry density, k = permeability; CH = clay with high plasticity; ML = silt with low plasticity

Table 3. Chemical properties of soils.

Property	HMSs	ARAs
pH (1:10 ratio)	6.22-7.35	4.23-4.45
Organic content, %	3.0-3.9	2.9-11.0
Carbonate content, %	8.0-12.9	3.9-15.0
SSA, m^2/g	20-36	12-16
CEC, meq/100g	1-6	1-9
Clay mineralogy	K, I, M	I, M

K = kaolinite; I = illite; M = montmorillonite

shows the existence of high illite mineral and low activity shows the existence of high kaolinite mineral (Skempton, 1953).

Murray et al. (1996) has classified material for use as a landfill barrier using the plasticity chart. Materials which were plotted below the A-line were defined as unsuitable, as materials with greater hydraulic conductivity e.g. sands and gravels. Clay with above the A-line was deemed suitable or marginal. According to the clay material plasticity classification scheme, using the chart shown in Murray et al. (1996), HMS soil samples are considered as "suitable" for use as a landfill barrier (Fig. 3).

HMS soil samples have the lowest permeability compared to ARA soil samples. The value of k = 10-9 m/secs indicates the approximate lower limit below which a soil may be considered "impervious" for all practical purpose.

Breakthrough curves and retention assessments via leaching column

Results of heavy metals concentration in the effluents (Ce) relative to the influent concentration (Co) are shown as breakthrough curves (Ce/Co). The breakthrough curves of Pb, Cu, Zn and Ni for two soils are depicted in Figures. 4(a), 4(b), 5(a) and 5(b). Considering breakthrough occurs when Ce/Co > 0.5, the test results shown in the figures indicate no breakthrough of heavy metals detected in the

effluents. It also may be noted that there are similarities in breakthrough profiles for Pb, Cu, Zn and Ni. However, Ni breakthrough profiles showed different pattern compared to Pb, Cu and Zn.

The pH values as depicted on the same figures (Figs. 4b and 5b) of the pore water (effluents) showed a range of pH3.5-pH4.0 for ARA soils and pH6.5-pH7.5 for HMS soils. The pH values of the effluents ARA soils indicate that these soils posses low buffering capacities and pH values of the effluents HMS soils indicate that these soils posses high buffering capacities.

The pH profiles remains constant after 5PV of leaching. This feature is significant and necessary for retardation of heavy metals via mechanisms of precipitation. Considering the results after the first 2PV in Figure. 4(b) and 5(b), it is seen that less than 50% of heavy metals are retained in the columns. The relative concentrations, Ce/Co for HMS soils recorded a range from 10-1 - 10-5 and Ce/Co for ARA soils range from 10-1 - 10-4.

Fig. 7 and Fig. 8 show the hydroxides and organics forms of Pb and Cu show the highest retention.

CONCLUSIONS

This study has shown that retention of heavy metals in HMS and ARA soil samples have same ranked order of buffering capacity; Cu>Zn>Pb>Ni. This corresponds with the pH of the effluents and the pore fluid
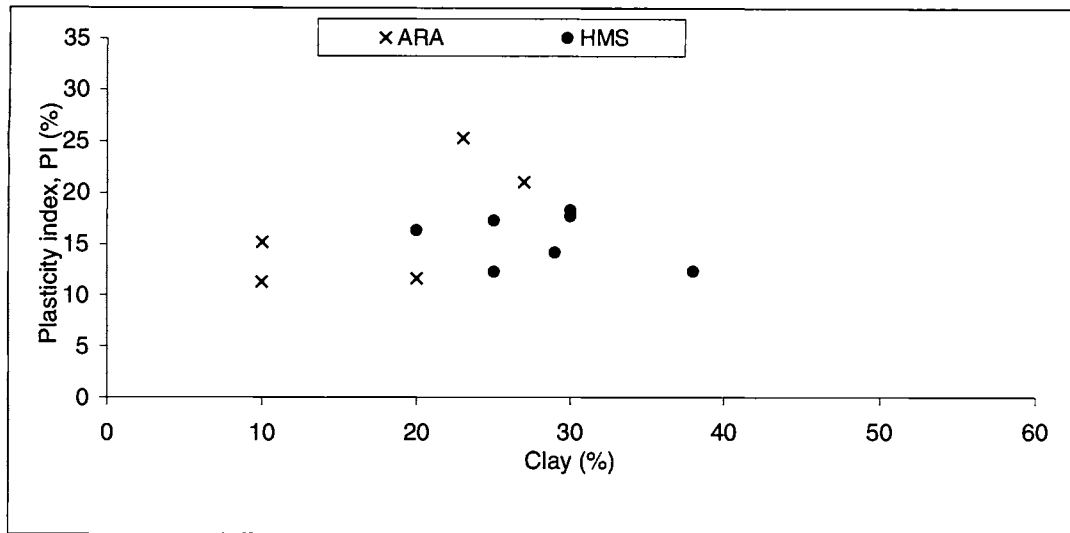
50

Figure 2. Clay activity chart showing mostly of soil samples have moderate to high clay activity.
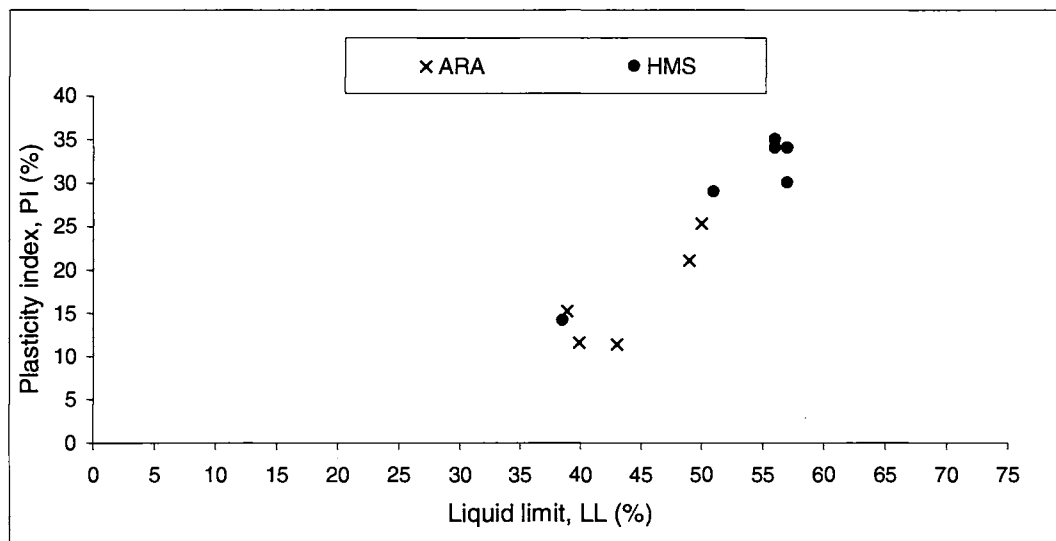

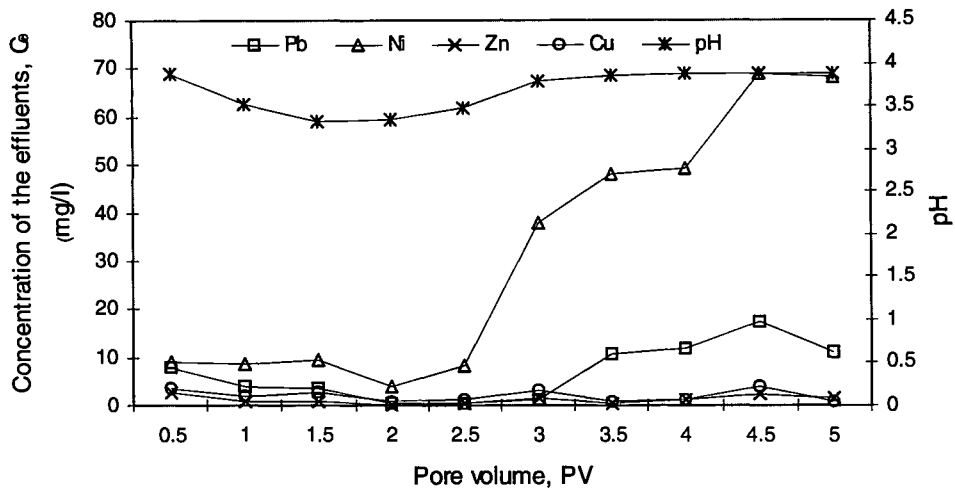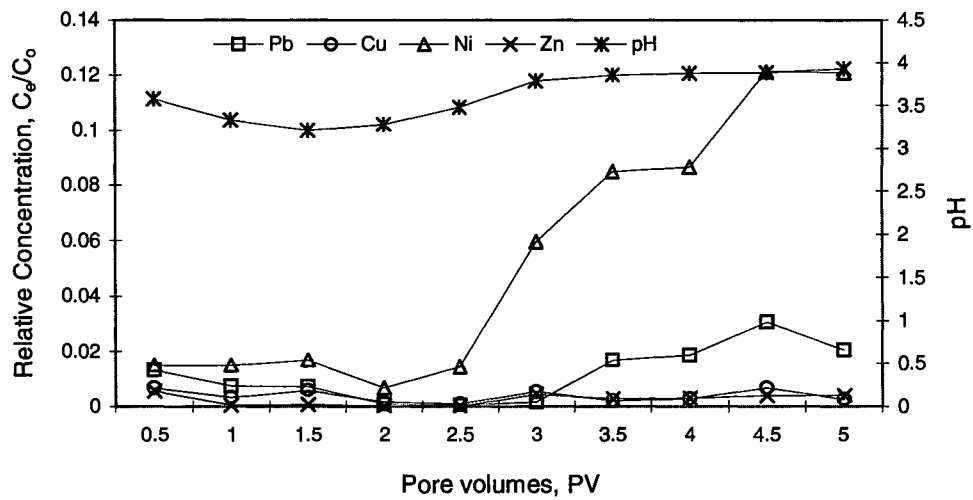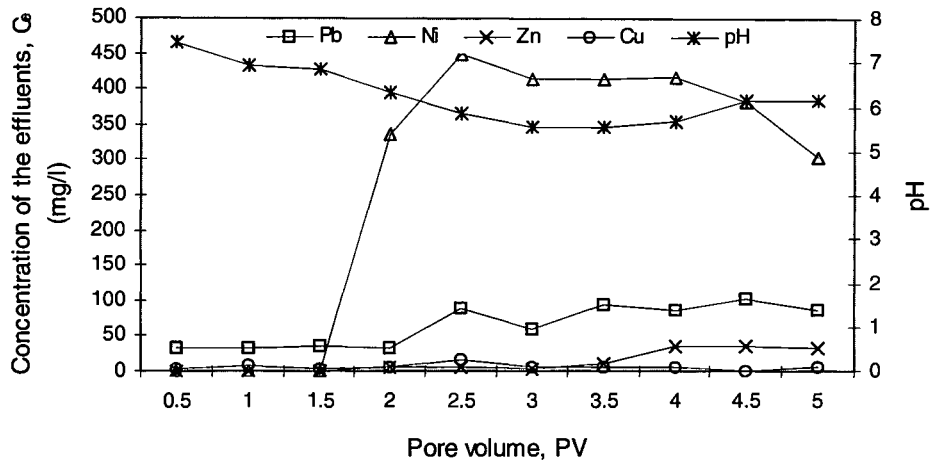Figure 3. Plasticity chart showing index properties of soils

Fig. 4. (a) (above) The profiles of absolute effluent concentration value (C_e) of Pb, Cu, Zn and Ni for sample ARA. Fig.4 (b) (below) The breakthrough curves for sample ARA for Pb, Cu, Zn and Ni and their relation with pH
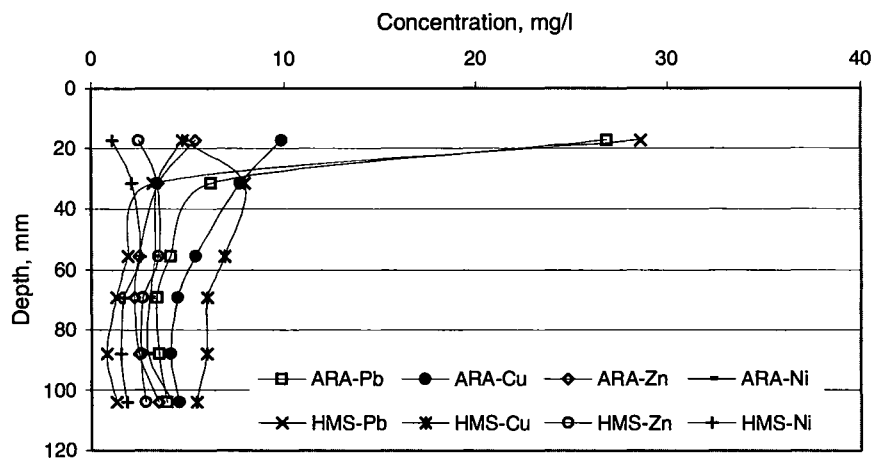
Fig. 5. (a) (above) The profiles of absolute effluent concentration value (C_e) of Pb, Cu, Zn and Ni for sample HMS. (b) (below) The breakthrough curves for sample HMS for Pb, Cu, Zn and Ni and their relation with pH.
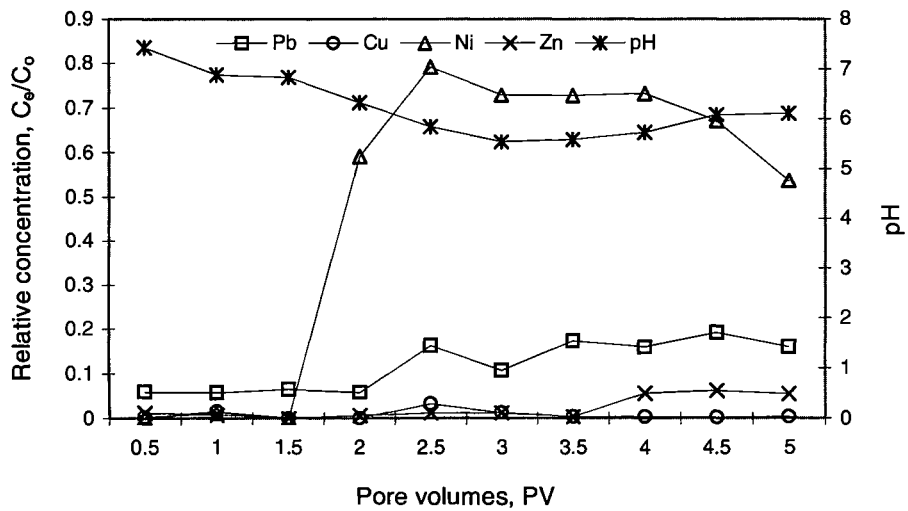
Fig. 6. The retention profiles of total Pb, Cu, Zn and Ni determined from acid digestion in samples ARA and HMS after 5PV leaching.
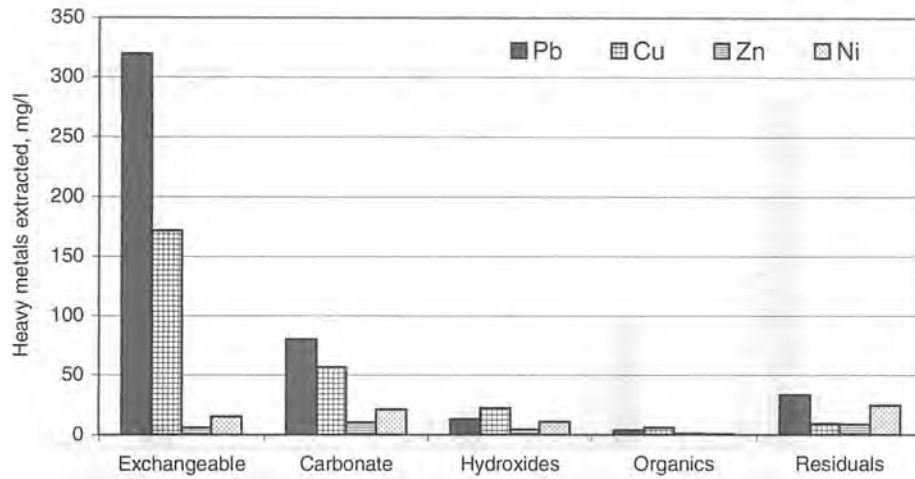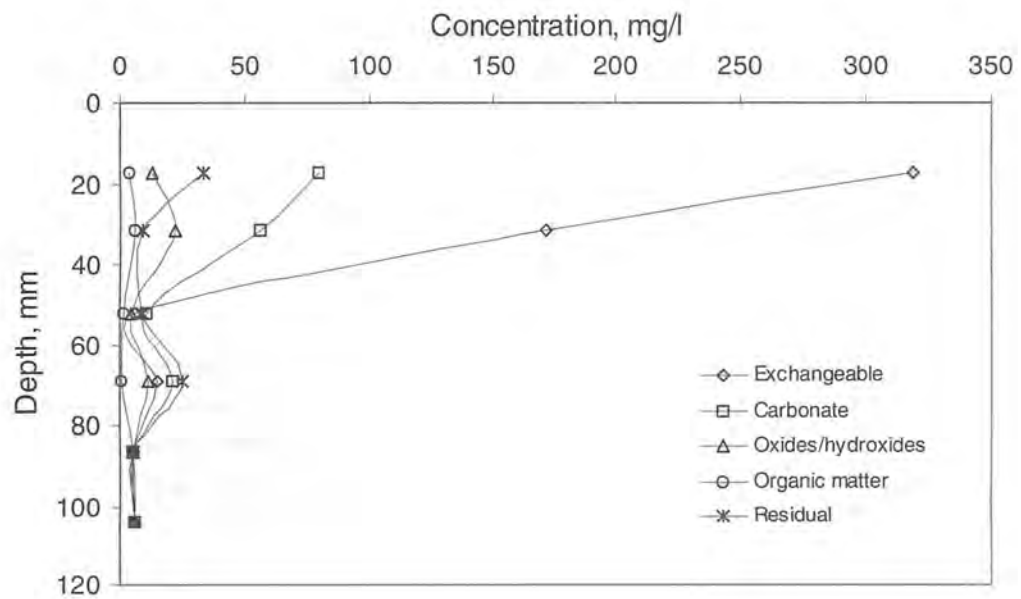
Fig. 7. (a) (above) Heavy metals extracted via SSE from ARA samples. (b) (below) The extraction profiles in ARA soils with depth.
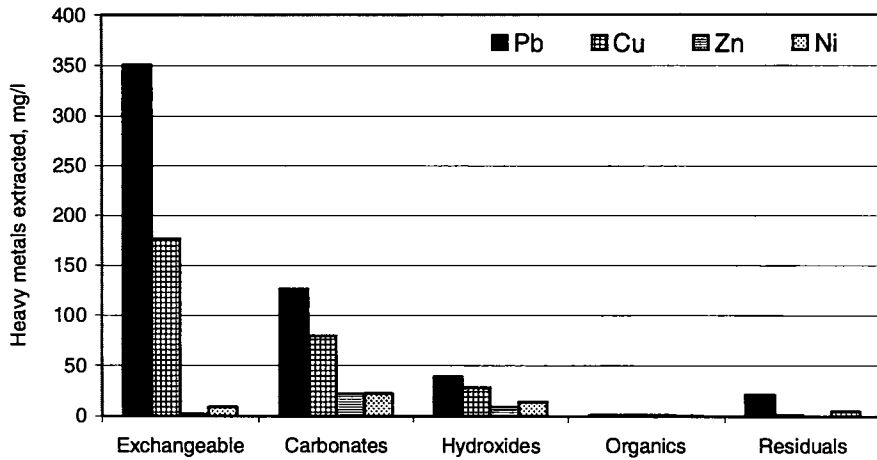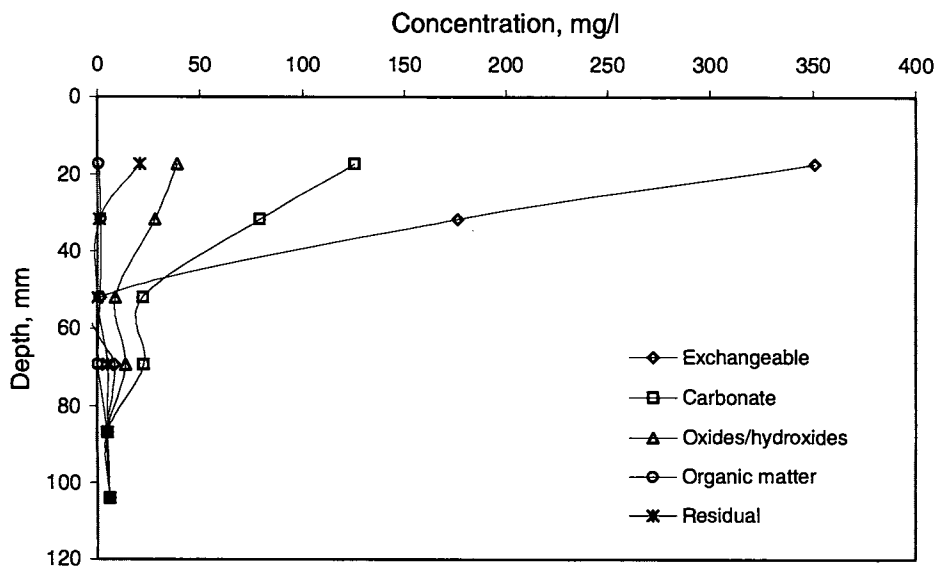
Fig.8. (a) (above) Heavy metals extracted via SSE from HMS samples. (b) (below) The extraction profiles in HMS soils with depth.

where HMS soils are more alkali compared to ARA soils. From SSE analysis, the retention mechanisms of the heavy metals in both of soil solids can be ranked in the following order: Exchangeable > Carbonates > Hydroxide > Residual > Organic. Although both of soil samples have same ranked order of buffering capacity and retention mechanisms of heavy metals, HMS soil samples is the best soil for lining material compared to ARA soil samples. Because of the high pH in the natural soils, the primary retention mechanisms for the HMS soils were precipitation of the heavy metals. The soils showed good buffering capability against very acidic leachate. This is a significant factor in favour of the use of such soils as clay barrier materials in landfill. The ability of these soils to maintain their pH is important to promote precipitation of heavy metals.

ACKNOWLEDGMENTS

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