Migration of heavy metals through compacted soil columns

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Abstract: Soils have different capability to function as engineered clay liner. The study was designed to evaluate the capability of soils for landfill liner materials and to investigate the behaviour of heavy metals in soils. The study has revealed that soil CEA3 has a better potential for liner material compared with soil MR1. Heavy metals are highly retained inside the soil particularly at the top part of the soil column, where Pb shows the highest retained in the soil column. Zn is more mobile compared with Cu and Pb. Confirmation studies of retention mechanisms using selective sequential extractions revealed that precipitation of heavy metals with carbonates and amorphous oxides/hydroxides was a dominant retention mechanism. This is followed by complexation with organic matter, adsorption into the soil mineral lattices and the ionic exchange onto the negatively charged of clay surfaces.

Abstrak: Tanah mempunyai kapasiti yang berbeza untuk berfungsi sebagai pelapik kejuruteraan lempung. Kajian ini bertujuan untuk menilai kebolehan tanah sebagai pelapik lempung dan juga untuk menyiasat sifat logam berat di dalam tanah. Kajian telah menjumpai bahawa tanah CEA3 mempunyai potensi yang lebih baik sebagai pelapik lempung berbanding dengan tanah MR1. Logam berat lebih banyak ditahan di bahagian atas turus tanah, di mana Pb paling banyak dibantutu dalam tanah. Zn pula adalah lebih mobil berbanding Cu dan Pb. Kajian pengesahan mekanisma penahanan logam berat menggunakan ujian ektraksi terpilih menunjukkan pemendakan logam berat dengan bahan berkapur dan bahan amorfus oksida/hidroksida merupakan mekanisma yang paling dominan. Ini diikuti oleh pengkopleksan dengan bahan organik, penjerapan ke dalam kekisi mineral primer, dan pertukaran ion di atas permukaan lempung yang bercas negatif.

INTRODUCTION

Landfill is regarded as the Best Practicable Environmental Option (BPEO) in disposing off municipal solid waste (DOE, 1995). Leachate and landfill gas have posed very dangerous treat to human health and the environment. Natural soils have been widely used as an engineering clay liner to impede the movements of the pollutants. The advantages of using clay liner are; (1) it is cheaper compared with other materials; (2) it is always available on-site; (3) it can react chemically to stop the flow of polluted leachate; and (4) react chemically to attenuate the pollutants species.

The purpose of this study is to assess the attenuation capability of natural clay soils in acting as part of the liner systems and to investigate the fate and behaviour of heavy metals in soils.

MATERIALS AND METHODS

Soil samples for this research were collected adjacent to active landfill sites in South Wales United Kingdom, namely estuarine alluvium soils from Cardiff (CEA3) and weathered mudrocks from Aberdere (MR1). There are two types of experiments that were utilized in this research; i.e. leaching column experiments and selective sequential extractions (SSE). In the leaching column experiment — Figure 1, the soil was compacted inside the plexiglass cylinder and was exposed to various types of heavy metal species. A real leachate was spiked with various heavy metals' nitrate solutions to increase their concentrations, so that soils can be assessed under extreme condition. The pH of the spiked leachate was reduced to 1.45 to increase the mobility of the heavy metals species in the leachate.
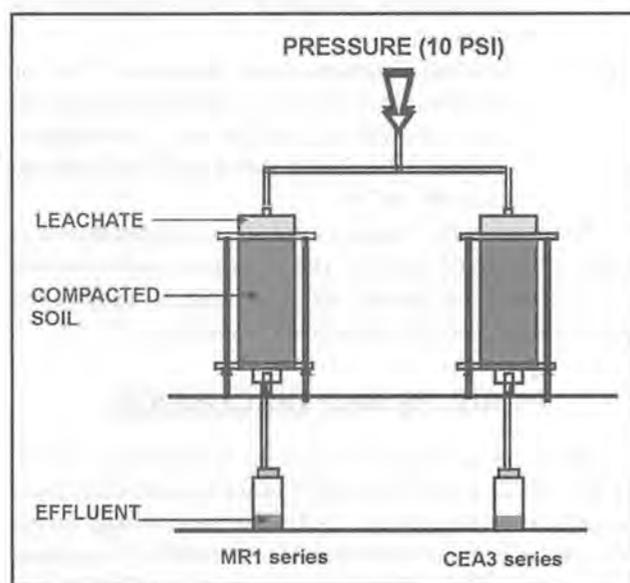

Figure 1. Two series of leaching column experiments.

The leachate was pushed into the soil using a pressure at 60 KPa to speed-up the time taken for the experiment. The effluents were collected periodically after 0.5 PV for analysis. After termination of the experiment, the soil was extruded and sliced into 6 equal slices for chemical analysis.

The "contaminated samples" from leaching experiment were utilized for selective sequential extraction (SSE) analysis. This experiment can be divided into 5 phases (stages), namely exchangeable phase, carbonate phase, hydroxide/oxide phase, organic phase, and residual phase. The basic principle of SSE analysis is the removal of sorbed heavy metals form individual soil fractions. Chemical reagents, which are chosen, are designed to selectively destroy the bonds between the heavy metal species and specific soil fractions.

The procedure for heavy metals extraction for the different sorption mechanisms is as follow (Gupta and Chen, 1975; Tessier et al., 1979; Yong and Phandungchewit, 1993; Yong et al., 2001):-

Stage 1 – Exchangeable Cations: 8 ml of 1M Potassium Nitrate, KNO3.

Stage 2 – Carbonate: 8 ml of 1M Sodium Acetate (NaOAc).

Stage 3 – Oxides and hydroxides: 20 ml of 0.04 M of Hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% (v/v) Acetic Acid (HOAc), agitated occasionally at 96±3°C for 6 hours.

Stage 4 – Organics: This extraction is divided into three phases:- Phase i: 3 ml of 0.02 M Nitric Acid (HNO_3) and 5 ml of 30% H_2O_2 adjusted to pH 2.0 with HNO_3 occasionally agitated for 2 hours at temperature 85±2°C. Phase ii: 3 ml of 30% H_2O_2 (at pH 2.0), intermittently agitated for 3 hours at the temperature 85±2°C. Phase iii: 5 ml of 3.2M Ammonium Acetate (NH_4OAc) in 20% (v/v) HNO_3, diluted to 20 ml, and continuously agitated at room temperature for 30 minutes.

Stage 5 – Residual Fractions (acid digestion): 5 ml of hydrofluoric acid (HF), 5 ml of aqua regia i.e., nitric acid (HNO_3) 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 centrifugation. The supernatant collected and analysed, and the residue left was washed, centrifuged again, and the second supernatant discarded.

RESULTS AND DISCUSSION

The graph in Figure 2 shows the breakthrough curves for Pb, Cu and Zn for sample estuarine alluvium from Cardiff, United Kingdom (CEA3). The breakthrough curves were plotted between relative concentration (Ce/Co) against pore volume (PV). Relative concentration (Ce/Co) is a ratio between concentration of heavy metals in the effluents and concentration of heavy metals in the tested leachate.

Breakthrough occurs if Ce/Co > 0.5. The permeability of this particular soil is 5.7x 10^{-10} m/sec. The pore volume (PV) is the volume to displace the volume of liquid within the soil solids.

Interesting to note that the Ce/Co values are very small, in the order of 10^{-2} to 10^{-3}. The values of Ce/Co for Pb and Cu were constant along the leaching process, indicating high retention of these two metals. Zn values increased after 2.5 pore volume of leaching, indicating high mobility of Zn (i.e. Zn capable to migrate through the soil column). The pH line was quite constant with the values between 7-8; indicating good buffering capacity of the soil (i.e. soil capable to resist changes by an acidic leachate).

Another example of breakthrough curves for different soil MR1 is shown in Figure 3. This soil is highly contrast with sample CEA3. K value for this soil is quite high 4.32 x 10^{-9} m/sec, resulting lesser time taken to complete the leaching process. Decreasing values of pH indicating poor buffering capacity against an acidic leachate. Zn breakthrough occurred after 2.5 PV of leaching. Pb and Cu required longer time to breakthrough, and they could breakthrough after 10-15 PV of leaching (i.e. more time is required to observe Pb and Cu to penetrate the compacted soil columns).

Figure 4 shows the plot of retention profiles, i.e. the total heavy metals retained inside the soil column after leaching experiments for sample CEA3. Heavy metals were retained by various types of retention mechanisms namely, ionic exchange, precipitation, adsorption, and complexation. The plot shows very clearly that the heavy metals (Pb, Cu, and Zn) were predominantly retained at the top part of the column (from 0-30 mm). The concentration of heavy metals decreased towards the bottom of the column (30-120 mm) with the value less than 0.3 mg/g. Pb was highly retained compared with Cu and Zn.

Figure 5 shows the plot of migration profiles for sample estuarine alluvium from Cardiff, United Kingdom (CEA3). Heavy metals migrate along the compacted soil in soluble form within the pore spaces in between the soil solid particles. The soluble heavy metals may provide information about the movement of heavy metals through the soil column. The graph shows that the heavy metals were migrated only up to 30 mm of the depth of the column and the concentration of metals migrated were small about 140 mg/L (0.14 mg/g). It is interesting to note that Zn showed the highest heavy metal migrated, meaning less retention of Zn inside the soil. On the other hand, Pb showed the lowest heavy metal migrated indicating that Pb was highly retained in side the column. The mobility of metals can be ranked as Zn>Cu>Pb.

The comparison between the retention profiles (from leaching column experiment) and extraction profiles (SSE analysis) is vital to proof that all chemical reagents used in the SSE analyses were adequate to release all heavy metals (Fig. 6). This may provide qualitatively to support the statement that all heavy metals retained can be extracted
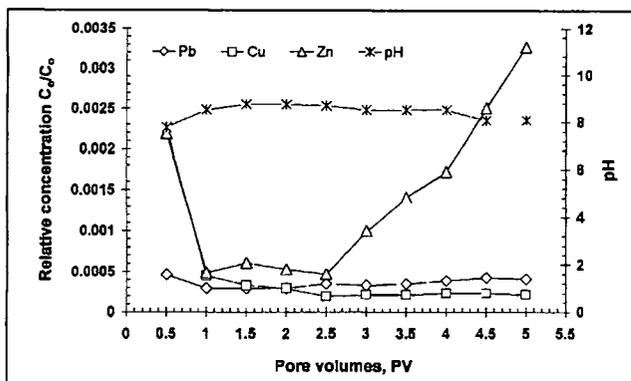
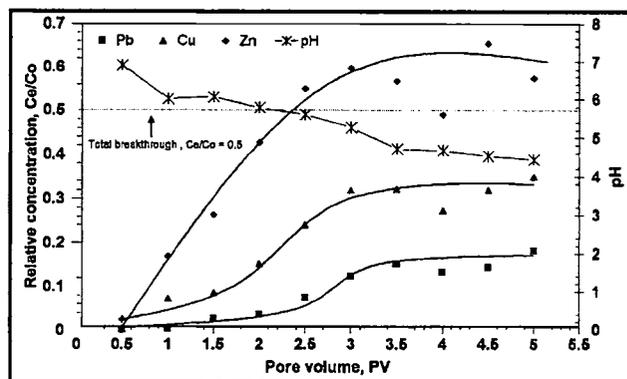**Figure 2.** The breakthrough curves for Pb, Cu and Zn for sample estuarine alluvium from Cardiff, United Kingdom (CEA3).

Figure 3. The breakthrough curves for Pb, Cu and Zn for sample weathered mudrock from Aberdere, United Kingdom (MR1).
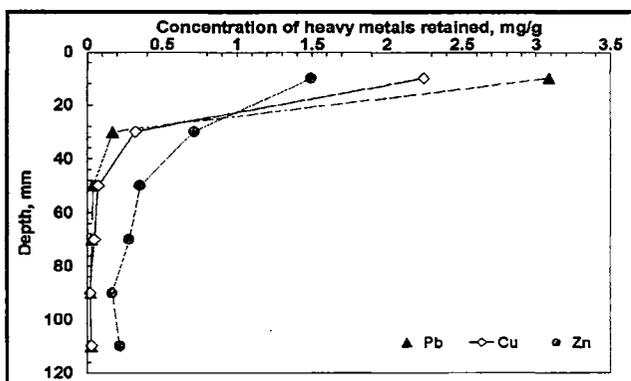

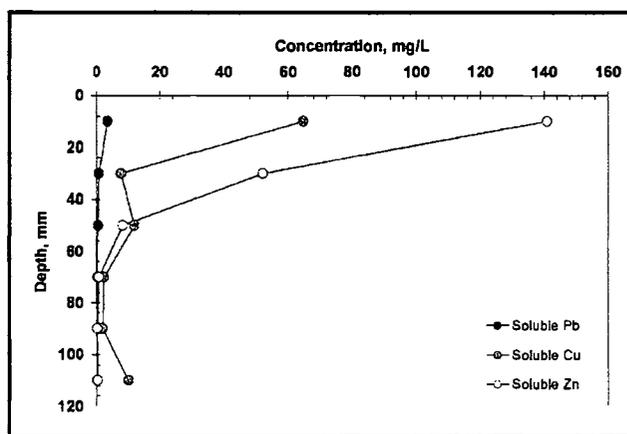**Figure 4.** Total Pb, Cu and Zn retained in compacted soil CEA3 after acid digestion analyses.

Figure 5. Soluble heavy metals in the pore fluid of soil CEA3 demonstrating relative mobility of heavy metals.
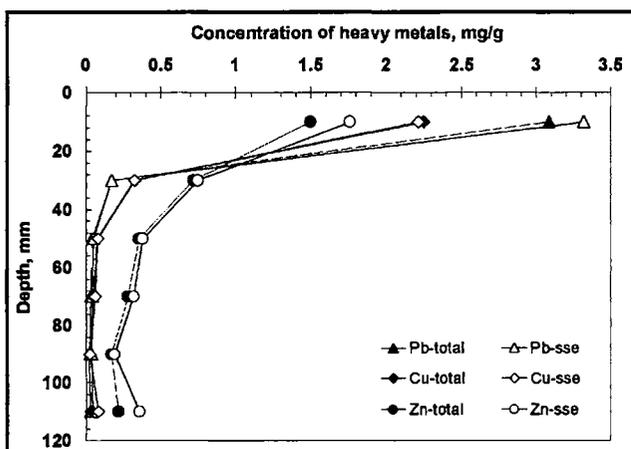

Figure 6. Comparison between the retention profiles (total heavy metals via acid digestions) and extraction profiles from SSE analyses for sample CEA3.
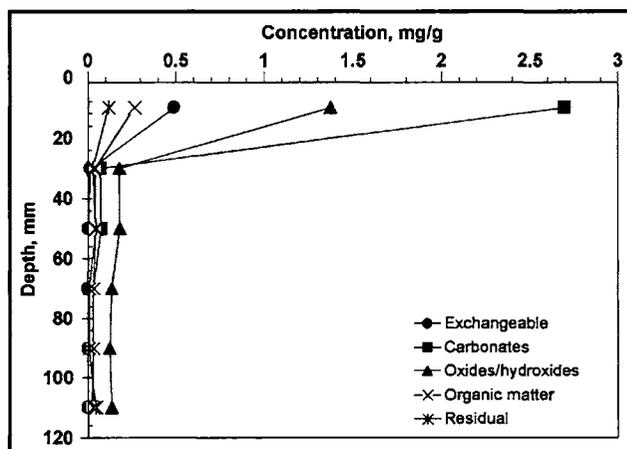

Figure 7. Pb extracted from various soil fractions in sample CEA3 after SSE analyses. Note that Pb was mainly retained in association with carbonate fraction.

back using various chemical reagents in SSE analyses. The graph also indicates that most of the heavy metals extracted from the top part of the column that corresponding very well with the retention profiles of the heavy metals.

Figure 7 shows that concentration of Pb extracted from different soil fractions. It can be seen that Pb is largely attached onto the carbonate phases with the values at the top was 2.7 mg/g. This is followed by oxides/hydroxide phase, organic phase, and residual fractions with the concentration less than 0.5 mg/g.

with organic materials, ionic exchange onto clay surfaces, and adsorption mechanisms into residual soil fractions.

ACKNOWLEDGEMENTS

CONCLUSIONS

The breakthrough curves reveal that estuarine alluvium soil from Cardiff (CEA3) is highly capable to function as engineered clay liner compared with weathered mudrocks from Aberdere (MR1). The retention profiles show that Pb is highly attenuated compared with Cu and Zn and these profiles are corresponded very well with the migration profiles where Zn is mobile and migrate more freely through the soil column compared with Cu and Pb. The extraction profiles have shown that the chemicals used in SSE analysis are capable to remove all heavy metals that were bound onto different soil fractions. SSE analyses reveal that most of the heavy metals were retained in association with carbonates and oxides/hydroxides fraction via precipitation mechanism. This is followed by complexation processes

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