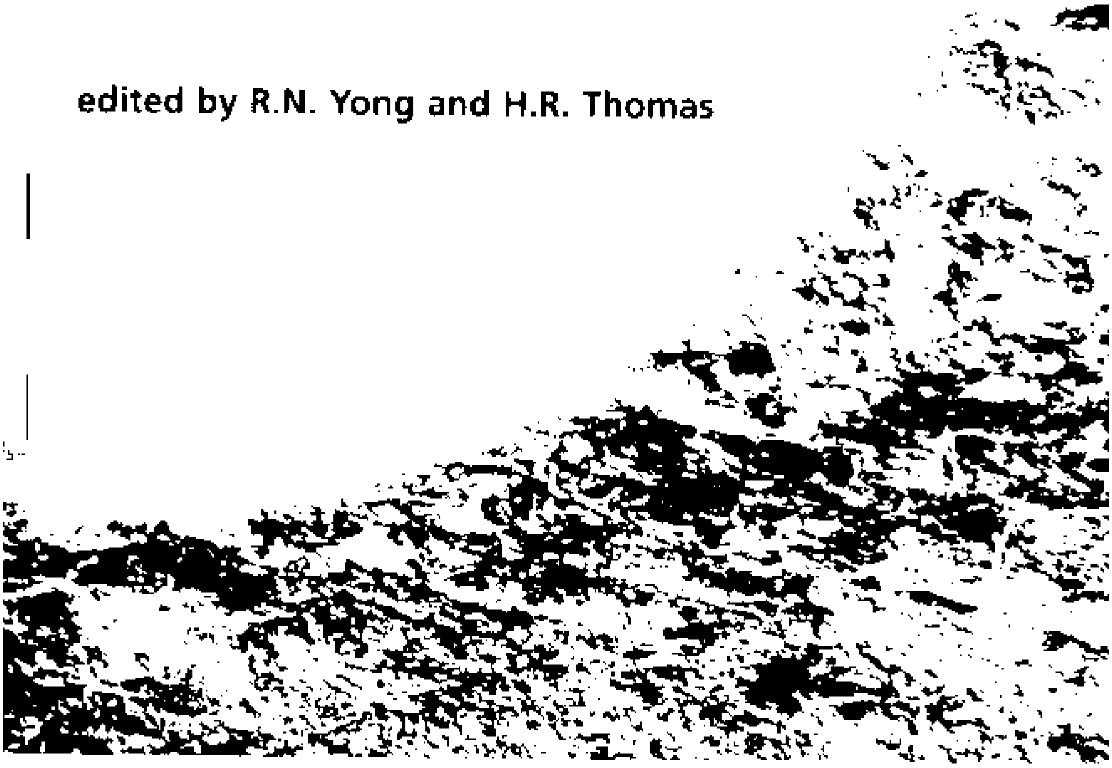
GEOENVIRONMENTAL ENGINEERING

Ground contamination: pollutant management and remediation

edited by R.N. Yong and H.R. Thomas



TRANSPORT, PERSISTENCE AND FATE OF POLLUTANTS

CONTAINMENT AND REMEDIATION

Examining competitive sorption of copper and nickel in London Clay with centrifuge leaching tests

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ABSTRACT

Sorption of contaminants on to soil constituents often has a significant effect on contaminant transport. The sorption equilibrium distribution coefficient, K_d, is often used in solute transport models when predicting the movement of a hazardous material in the ground, to calculate a retardation factor, R_d, for the contaminant. Centrifuge leaching tests were conducted to directly study the transport of Cu and of Ni, both singly and in combination, through compacted London Clay. The study used a falling head permeameter-style leaching apparatus in a laboratory centrifuge, simulating the migration of these heavy metals from landfill leachate through this low permeability clay. R_d was estimated from the breakthrough curves. Competitive sorption was found to have an important effect on the transport, causing the mobility of Ni in the London Clay to be significantly higher when present with Cu than when present on its own. The mobility of Cu was also higher when present with Ni, but the difference was less significant.

INTRODUCTION

Predicting the fate and transport of contaminants in natural soils and compacted clay barriers is a complex problem that requires an understanding and quantification of several processes such as advection, diffusion, dispersion, sorption, complexation, precipitation and filtration. The pattern of contamination in contaminated land and wastes is generally complex, with mixtures of different organic and inorganic materials often encountered. Heavy metals form a group of contaminants common in waste leachates (Sharma and Lewis, 1994) and many of them constitute a significant health hazard because of their toxicity. One important process affecting heavy metal mobility in soil is competitive sorption, in which the soil solids preferentially sorb one solute instead of another, which is therefore more mobile than if it alone were present.

The Geoenvironmental Research Centre is currently undertaking an experimental investigation quantifying the effect of competitive sorption on the mobility of selected heavy metals in London Clay. The investigation uses a laboratory centrifuge to conduct large hydraulic gradient leaching tests on compacted clay, with leachate sampling to determine breakthrough curves. The purpose of this paper is to present initial leaching test results for Cu and Ni, both singly and in combination, demonstrating the impact of competitive sorption on heavy metal mobility in this clay.

BACKGROUND

Sorption of metals is a competitive process between ions in solution and those sorbed on to the soil surface through either electrostatic attraction or surface complexation. As a result, pore

Geoenvironmental engineering, Thomas Telford, London, 1999, 296–301

water chemistry strongly affects ion retention on soil solids (Echeverría *et al.*, 1998), and therefore mobility, since strongly retained metals ions are removed from the pore water and become less mobile than weakly retained ions. Griffin and Au (1977) found that the amount of lead adsorbed by a calcium montmorillonite was dependent on the ratio of the equilibrium concentrations of the two exchanging cations and not upon the actual concentrations in solution, a result which is consistent with Boyd *et al.*'s (1947) expression for a competitive Langmuir adsorption equation. Kuo and Baker (1980) reported that sorption of Cu, Cd and Zn by three acid surface soils increased with increasing pH at low pH, Cu being preferentially sorbed over Zn and Cd, such that the presence of Cu interfered strongly with the sorption of the other two heavy metals.

Contaminant mobility is often estimated from sorption characteristics quantified by batch equilibrium experiments on soil suspensions. If adsorption of contaminants by the solid phases in soil is to be modelled, the applicability of terms which describe adsorption from soil suspension studies needs to be examined. Leaching column tests are more representative of natural conditions, but are technically more challenging to run and, for low hydraulic conductivity soils, very time consuming. Comparison between batch equilibrium and leaching column experiments gives mixed results even in low sorption capacity soils (Grolimund *et al.*, 1995; Yong *et al.*, 1992).

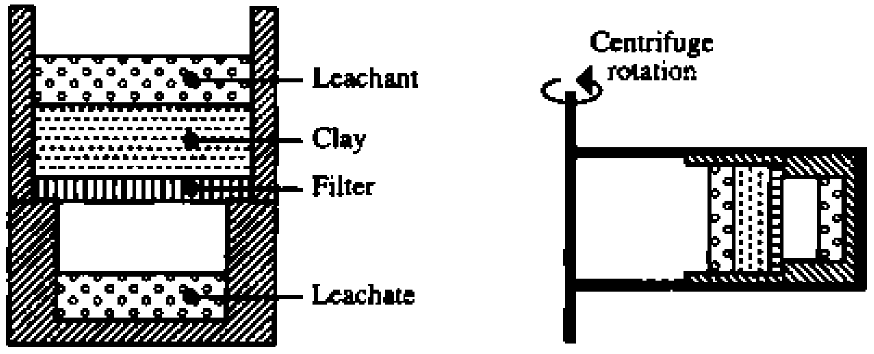
Small, laboratory centrifuges and large, geotechnical centrifuges have both become widely used to study the migration patterns of contaminants in soil, for a range of practical and scientific applications (Mitchell, 1998). In particular, centrifuges permit the systematic examination of the relative importance of different mechanisms in contaminant transport under controlled and reproducible testing conditions. Centrifuge leaching tests have shown great promise for the experimental study of reactive contaminant transport processes in fine-grained soils (Celorie *et al.*, 1989; McKinley *et al.*, 1998), because they greatly increase the fluid flow rate through compacted soils using relatively simple apparatus. As Mitchell (1998) points out, a centrifuge leaching test sample is subjected to an effective stress regime similar to that in the field but scaled in length and so has a lower risk of boundary leakage than if the sample were simply subjected to a large hydraulic gradient.

MATERIALS AND METHODS

London Clay was chosen for use in this study. London Clay is a stiff to very stiff, fissured clay with a hydraulic conductivity between 10^{-10} and 10^{-12} m/s (Chandler *et al.*, 1990; Dewhurst *et al.*, 1998). Blocks of the soil were recovered from tunnelling work below the Thames in Westminster, central London. X-ray diffraction analysis indicates that the principal minerals in the recovered samples are quartz, kaolinite, montmorillonite and muscovite. Of these, the montmorillonite will have the biggest influence on the sorption of heavy metals from solution, because it has a high surface area and a high cation exchange capacity. The blocks of clay were then broken up, allowed to dry in air, and crushed to a fine powder.

Three leaching tests on compacted London Clay have been conducted, one using a solution of 500 mg/L Cu as $Cu(NO_3)_2$, one using a solution of 500 mg/L Ni as $Ni(NO_3)_2$, and one using a solution of 500 mg/L Cu and 500 mg/L Ni as their nitrates. Figure 1 shows the centrifuge leaching cell used for this study. The cell has an upper section with a porous base, which retains the soil, and a lower section within which the leachate collects. In use, the cell resembles a falling head permeameter. The centrifuge equipment permits four such leaching cells to be used at once. Dried clay was slurried with deionised water, left overnight and then placed in the leaching cell. The four cells were centrifuged at 5285 gravities until one pore volume was collected, producing a layer of compacted clay on the porous filter. This took approximately two hour, typically. The supernatant fluid was then replaced with leachant solutions and leaching tests were performed at 5285 gravities and 21°C. Periodically, fresh leachant was added to the top of the cell to replace fluid passing through the clay, the collected leachate being removed at the same time. This leachate was acidified with 5% nitric acid for storage, and the heavy metal content determined by ICP-AES. Duplicate tests were conducted to examine variability.

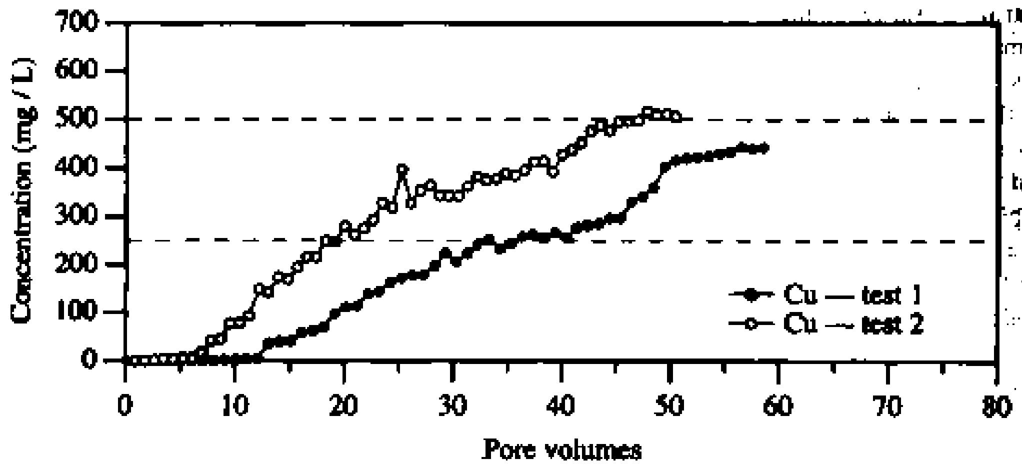
Figure 1. Centrifuge leaching cell



(a) Leaching cell design

(b) Leaching cell in use

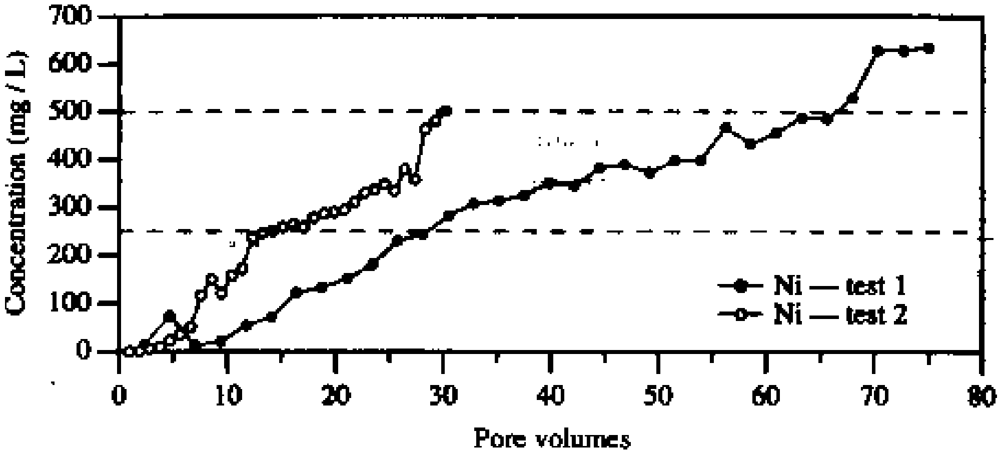
Figure 2. Breakthrough curves for Cu, influent 500 mg/L Cu



RESULTS AND DISCUSSION

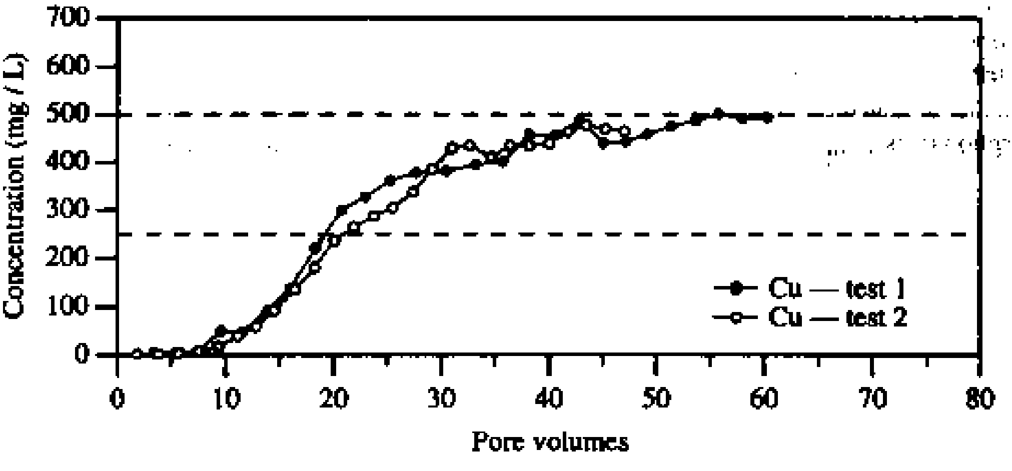
Figures 2 and 3 show the breakthrough curves for the leaching of 500 mg/L Cu and of 500 mg/L Ni through London Clay, respectively. Although both duplicates were mixed from the same sample, prepared in the same apparatus, and tested at the same time under the same conditions, there is still a considerable difference in the variation in effluent concentration with the number of pore volumes. Moreover, each duplicate was tested for the same length of time, so it is clear that the first clay specimen for Cu had a slightly higher hydraulic conductivity than did the second, while the first clay specimen for Ni had a hydraulic conductivity about twice that of the second. Time constraints meant that neither test could be run for significantly longer than the time taken to reach the leachant concentration, marked on the figures by the upper dashed line.

Figure 3. Breakthrough curves for Ni, influent 500 mg/L Ni



The number of pore volumes required for the leachate concentration to rise to half of the leachant concentration is a measure of the mobility of the contaminant, being approximately equal to the retardation factor (Shackelford and Redmond, 1995). For these tests, this level corresponds to 250 mg/L, which is shown on the graphs by the lower dashed line. For Cu, 20 pore volumes are required in one duplicate and 35 in the other, while for Ni 15 and 28 pore volumes are required. This suggests that Cu sorbs slightly more strongly to the clay than Ni does.

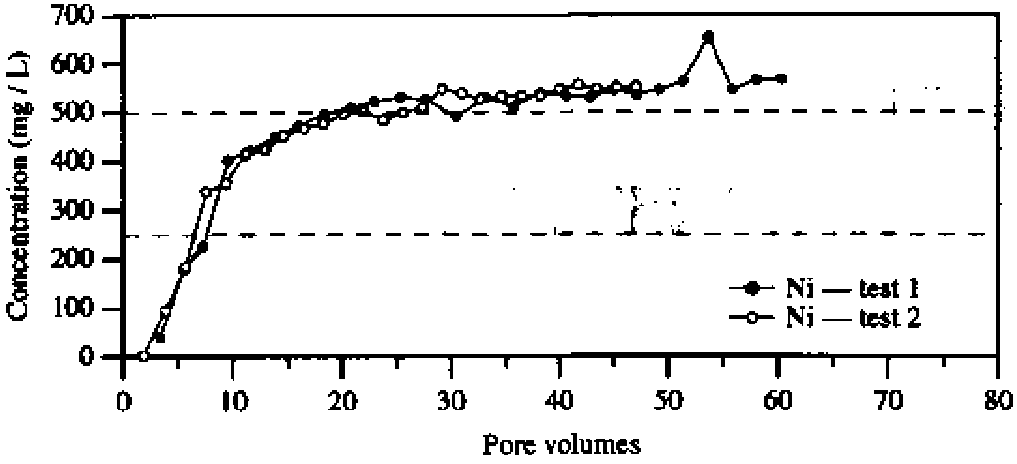
Figure 4. Breakthrough curves for Cu, influent 500 mg/L Cu + 500 mg/L Ni



Figures 4 and 5 show the breakthrough curves for Cu and Ni, respectively, when both are present in the leachant at 500 mg/L. There is now excellent agreement between each of the two duplicate tests, with the leachate concentration rising to steady values similar to those in the leachant. Approximately 20 pore volumes are required for the Cu concentration to rise to 250 mg/L, which is equal to the lower of the two values found for Cu on its own. In contrast, approximately 7 pore volumes are required for the Ni concentration to rise to 250 mg/L, compared to 15 and 28 for Ni on its own. This indicates that in the presence of

Ni the mobility of Cu is increased only slightly, if at all, while in the presence of Cu the mobility of Ni is increased by a factor of 2–4. Cu appears to be sorbing preferentially on to the soil, which is consistent with the observation from the single contaminant leaching tests that Cu appears to bond more strongly with the clay than Ni does. Competitive sorption effects are therefore having a significant effect on the migration rate of the less preferred heavy metal, behaviour similar to that noted by Alloway (1997) for surface soils.

Figure 5. Breakthrough curves for Ni, influent 500 mg/L Cu + 500 mg/L Ni



The work reported here is part of an on-going research project to examine Cu, Ni and Zn mobility in London Clay and the effect of competitive sorption. The results here are from the development stages of this project, which may account for the variation between the duplicate tests for each single element. Any conclusions drawn from the results are therefore preliminary, and additional analysis of this data is needed. Tests at lower centrifuge speeds are also planned, providing data on the dependence of mobility on leachant flow rate. The apparent distribution coefficients calculated from the breakthrough will be extrapolated to zero flow rate, and the estimated distribution coefficients compared with those measured in conventional batch sorption tests.

CONCLUSIONS

The rate of migration of Cu and Ni, individually and in combination, through compacted London Clay has been successfully measured using a permeameter style leaching cell in a laboratory centrifuge. The centrifuge technique provides the opportunity to simulate confining stresses similar to those in a natural soil deposit. For the first tests conducted as part of this on-going research project, in which the heavy metals were present in the leachant on their own as nitrates, 20–35 pore volumes of flow were needed for the Cu concentration in the leachate to rise to half of the leachant value, while 15–28 pore volumes were needed for the Ni concentration to rise to this level. In the second test, where both heavy metals were present in the leachant, the number of pore volumes required to reach half of the leachant value was 20 for Cu and 7 for Ni. This indicates that the presence of the preferentially sorbed Cu ion has interfered with the sorption of the Ni ion on to the soil solids and resulted in a two to fourfold increase in the migration rate of Ni.

ACKNOWLEDGEMENTS

This work is sponsored by the Engineering and Physical Sciences Research Council, grant number GR/M27067. This support is gratefully acknowledged.

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