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LEACHING TESTS IN A LABORATIRY CENTRIFUGE ON ZINC MIGRATION IN LONDON CLAY

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Abstract

Sorption of contaminants onto soil constituents often has a significant effect on contaminant transport. The retardation factor, R_d*, is often used as an indication of the mobility of the contaminant. Centrifuge leaching tests were conducted to directly study the transport of Zn, through compacted London Clay. The study used a falling head permeameter-style leaching apparatus in a laboratory centrifuge, simulating the migration of this heavy metal from landfill leachate through this low permeability clay. Centrifuge acceleration in the range of 1300 to 5280 gravities were used in order to attempt a prediction of the Zn mobility in real field conditions.* R_d *was estimated from the breakthrough curves and was compared with batch test findings on the same soil. Increasing centrifuge acceleration was found to have an important effect on the sorption onto soil, and thus on transport, causing the mobility of Zn in the London Clay to be significantly higher at higher gravities.*

Key words: zinc, laboratory centrifuges, contaminant mobility, retardation factor, scaling

Résumé : Essais de lessivage dans une centrifugeuse de laboratoire sur le transport de zinc au travers d'une argile "London Clay"

La sorption des contaminants sur les constituants du sol a souvent un effet important sur leur transport. Le facteur retardant, R_d*, est souvent utilisé comme indicateur de mobilité du contaminant. Des essais de lessivage en centrifugeuse ont été réalisés afin de permettre une étude directe du transport de Zn au travers d'une London Clay. L'étude a utilisé un appareil de lessivage de type perméamètre à charge variable dans une centrifugeuse de laboratoire, simulant la migration de ce métal lourd à partir d'un filtre de décharge au travers de cette argile à faible perméabilité. Une accélération centrifuge comprise entre 1300 et 5280 gravités a été utiliseé afin de tenter de prédire la mobilité du Zn dans des conditions réelles.* R_d *a été estimé à partir des courbes "breakthrough curve" et cette valeur a été comparée avec les résultats obtenus sur des essais "batch" effectués sur le même sol. On a pu remarqué qu'une accélération centrifuge croissante avait un impact important sur la sorption sur le sol, et donc sur le transport, ceci ayant pour conséquence une mobilité du Zn dans la London Clay beaucoup plus importante pour les hautes gravités.*

Mots clés: zinc, centrifugeuse de laboratoire, mobilité des contaminants, facteur retardant, facteur d'échelle

1. 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 [1] and many of them constitute a significant health hazard because of their toxicity [2]. One important process affecting heavy

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metal mobility in soil is sorption. Partitioning of heavy metal ions between the soil solution and the soil solids reduces the mobility of the metal contaminants.

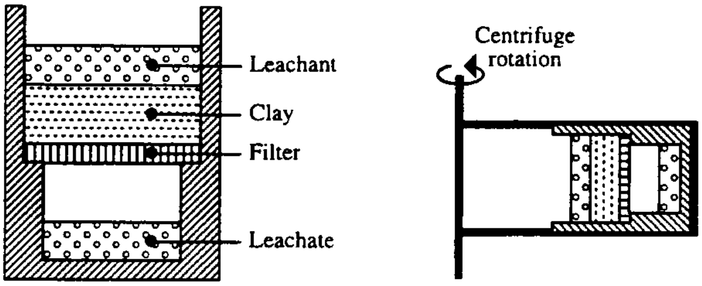
The Geoenvironmental Research Centre is currently undertaking an experimental investigation quantifying the effect of different acceleration levels on sorption, and the effects that this has on the mobility of selected heavy metals in London Clay. The investigation uses a laboratory centrifuge to conduct 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 Zn, demonstrating the impact of movement scaling on heavy metal mobility in this clay.

Sorption of metals onto soil solids 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 water chemistry strongly affects ion retention on soil solids [3], and therefore mobility, since strongly retained metals ions are removed from the pore water and become less mobile than weakly retained ions. 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. Celorie *et al.* [4] reported that batch tests tend to overestimate the sorption efficiency of soils, and therefore underestimate the mobility of contaminants, especially at low solute concentrations. This is of great geo-environmental importance since risks of heavy metal contamination would not be properly assessed if decision making relies only on measurements conducted with batch tests. Comparison between batch equilibrium and leaching column experiments gives mixed results even in low sorption capacity soils ([5], [6]).

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 [7]. 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 ([8], [9]), because they greatly increase the fluid flow rate through compacted soils using relatively simple apparatus. As Mitchell [7] 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.

1. 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 ([10], [11]). 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 a and crushed to a fine powder.



Leaching cell **Leaching cell in use**

Figure 1: Centrifuge leaching cell.

Three leaching tests on compacted London Clay have been conducted, using a solution 500 mg/L Zn as $Zn(NO_3)_2$. The leachant solution was not adjusted to a particular pH, but w found to have pH of 5·0. Figure 1 shows the centrifuge leaching cell used for this study.

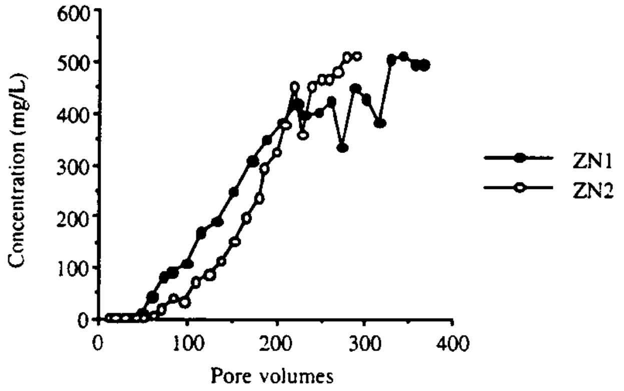


Figure 2: Zinc breakthrough curve at 1300 gravities.

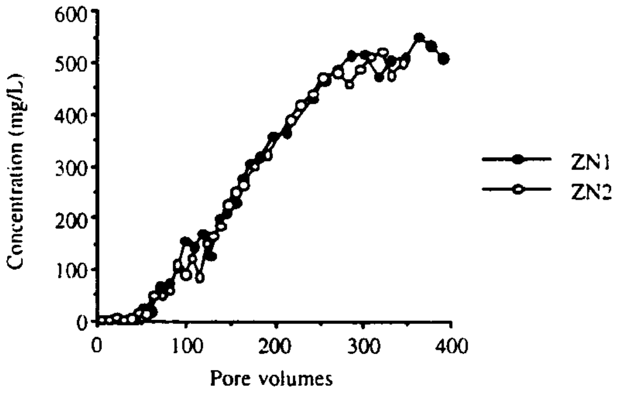


Figure 3: Zinc breakthrough curve at 2600 gravities.

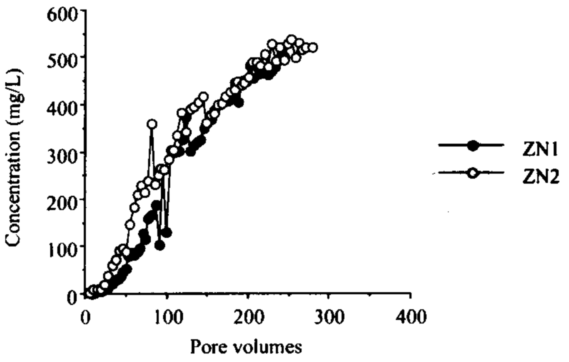


Figure 4: Zinc breakthrough curve at 5280 gravities.

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 three different gravity levels: 5280, 2600 and 1300 gravities. Initially the cells ran until one pore volume was collected, producing a layer of compacted clay on the porous filter. This took approximately two hours, typically, for the high speed, and three hours for the medium and low speed. The centrifuge was then stopped, the supernatant fluid was replaced with leachant solutions and leaching tests were performed at the three gravity levels at 21°C. Periodically, the centrifuge was stopped and 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. The volume of soil used was small, to permit leaching tests to be conducted on this low permeability material in a reasonable time: the compacted layer of clay was only 3mm thick.

3. Results and Discussion

3.1 Centrifuge Tests

Figures 2, 3 and 4 show the breakthrough curves for the leaching of 500 mg/L Zn through London Clay at escalating acceleration levels. In order to account for the natural soil variability two replicates were used for each acceleration level run. The replications were very close at all three gravities. The number of pore volumes required for the leachate concentration to rise to half of the leachant concentration is a simple measure of the mobility of the contaminant, being approximately equal to the retardation factor, R_d [12]. R_d is a measure of the metal mobility in the soils, which represents the retardation of the solute movement compared to the water movement, in which it is dissolved. The higher the R_d, the lower the mobility of the metal. For these tests, this level corresponds to 250 mg/L. Although this approximation would be particularly valid in case of equilibrium conditions, the shape of the breakthrough curves indicate an asymmetrical pattern, which is characteristic of a non-equilibrium system [13]. Although this way of measuring the R_d value can be successful under these conditions ([4], [14]), the retardation factor was instead estimated using the breakthrough curve fitting program CXTFIT [15]. The pH of the leachate was sampled at intervals, and found to change only slightly, from an initial value of 7·4 to around 7·1, as leaching progressed.

It was found that the mobility of Zn increased with the increased acceleration level. The R_d value at 5280 gravities was 108±10, while at 2600 gravities it was 165±3 and at 1300 gravities it was 184±12. This is probably due to the metal having less time to interact with the soil surfaces at high acceleration levels than at lower acceleration levels. This reduced the adsorption of Zn onto the soil, and thus its mobility was enhanced at 5280 gravities. This reduced mobility indicates that there is a scaling effect, which affects the Zn mobility significantly. The R_d values calculated from the number of pore required to reach a concentration of 250 mg/L were slightly lower at each speed than these values, and were not used.

By extrapolating the data series to unit gravity (the gravity level at field conditions) there is an R_d value that could be estimated, although this extrapolation is necessarily difficult given the range of accelerations which must be employed. Figure 5 shows the R_d values calculated from the centrifuge leaching tests at the different gravity levels. The extrapolated value provides a valid indication of the metal mobility through the London Clay in the field and is $R_d = 196$ for a parabolic extrapolation and $R_d = 212$ for a linear one. There is insufficient data to determine the most appropriate extrapolation scheme.

3.2 Batch tests

Batch tests were performed on the London Clay. Zinc was added to test tubes in a range of concentrations of 1–3920 mg/L (Table I). The data were fitted to the Langmuir model. Then, the partitioning coefficient, K_d, was calculated from the Langmuir model fit. (K_d was found to be 98·9 mL/g). Using this K_d value, it is difficult to calculate an R_d value. This is because there are several ways of calculating K_d. One way is given by the 'classic' formula:

$$R_d = 1 + \frac{\rho_b}{n} K_d \qquad (1)$$

where ρ_b is the dry bulk density and n is the porosity of the sample [16]. Following this formula, R_d was found to be 199.

A second way of calculating R_d was suggested by Fetter [17]. This introduces a correction factor, which accounts for the higher equilibrium solution concentrations (because the K_d calculated from the Langmuir model assumes low equilibrium solution concentrations).

The formula to calculate R_d from a given K_d is:

$$R_d = 1 + \frac{\rho_b}{n} \frac{K_d}{(1 + kC)^2} \qquad (2)$$

where k is a constant calculated from the Langmuir equation and C is the equilibrium metal concentration in the solution. C was chosen to be 250 mg/L; this concentration is significant, because it defines the R_d value in the breakthrough curves. The value of R_d found was now 25.

However, there is a third way of calculating an R_d value. This follows a different way of calculating K_d from the batch test data and does not use the model fit. This method measures directly the 'equivalent' S/C value (where S is the equilibrium concentration of sorbed Zn (in mg/g)) from the batch data plot for a given C value, which was chosen to be 250 mg/L. K_d as now found to be 21. The R_d was then calculated using the formula (1). By this procedure the R_d value obtained is 43.

In Figure 5 the dashed lines represent the upper and lower R_d values found using from the batch test data, *i.e.* using the first two procedures. It can be noted that the values measured in the centrifuge leaching tests lie between these two values, with the R_d obtained from formula (1) being just higher than the range of values obtained from the centrifuge leaching tests. However, it can be noted that the R_d values estimated from the batch data vary remarkably, depending on what method one uses to calculate it. This increases the uncertainty regarding the mobility of Zn (and subsequently, of other heavy metals as well) in normal field conditions. On the other hand, centrifuge tests minimise this risk of misinterpreting data, because the way to calculate R_d is easy to determine.

Zn concentration in solution (C) (mg/L)	Concentration of sorbed Zn (S) (mg/g)
3920	13·6
1540	12·1
49	3·5
11·5	1·8
1·0	0·7

Table 1: Data from the batch test.

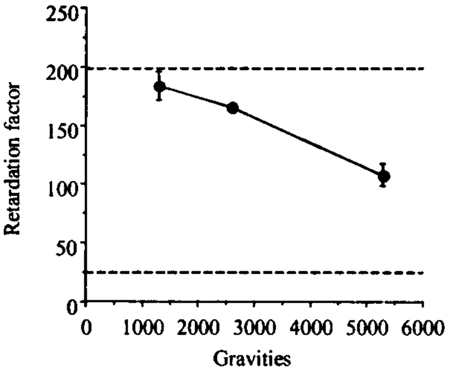


Figure 5: Scaling of the R_d values obtained by the breakthrough curves, compared with the R_d values obtained directly from the batch tests (dashed line).

4. Conclusions

The rate of migration of Zn 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.

Th R_d values obtained from the centrifuge tests were 108±10, 165±3 and 184±12 for gravity levels of 5280, 2600 and 1300, respectively. The fact that Zn mobility was affected by the acceleration level of the leachant solution indicates that there is a scaling effect in the movement of Zn. This means that R_d values for heavy metals can be extrapolated to unit gravity, although with some care, where this gravity level represents real field conditions. However, more experimental evidence is needed for this to be performed and before safer conclusions might be drawn. This is an on-going research project, where more such data are produced in order to assess this procedure. Nevertheless, given the scarcity of satisfactory data on heavy metal mobility in UK soils, especially in low permeability soils where mobility tests with leaching columns would take a very long time to perform, high speed laboratory centrifuge tests can be valuable for the quantification of heavy metal mobility in field conditions.

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