detritus | Multidisciplinary Journal for Waste Resources & Residues

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THE ROLE OF NATURAL CLAYS IN THE SUSTAINABILITY OF LANDFILL LINERS

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Article Info:
Received:
26 November 2019
Revised:
12 March 2020
Accepted:
27 April 2020
Available online:
8 May 2020

Keywords:
Chemical compatibility
Compacted clays
Attenuation
Landfill liners
Leachate pollutants

ABSTRACT

Engineered synthetic liners on their own cannot protect the environment and human health against landfill leachate pollution. Despite their initial impermeability, they are susceptible to failure during and after installation and have no attenuation properties. Conversely, natural clay liners can attenuate leachate pollutants by sorption, redox transformations, biodegradation, precipitation, and filtration, decreasing the pollutant flux. Depending on the clay, significant differences exist in their shrinkage potential, sorption capacity, erosion resistance and permeability to fluids, which affects the suitability and performance of the potential clay liner. Here, the physico-chemical, mineralogical and geotechnical characteristics of four natural clayey substrata were compared to discuss their feasibility as landfill liners. To study their chemical compatibility with leachate and rainwater, hydraulic conductivities were measured every ≈2 days spread over 7 weeks of centrifugation at 25 gravities. At field-scale, this is equivalent to every 3.4 yrs spread over 80 yrs. All the clayey substrata had favourable properties for the attenuation of leachate pollutants, although different management options should be applied for each one. London Clay (smectite-rich) is the best material based on the sorption capacity, hydraulic conductivity and low erodibility, but has the greatest susceptibility to excessive shrinkage and alterable clay minerals that partially collapse to illitic structures. Oxford Clay (illite rich) is the best material for buffering acid leachates and supporting degradation of organic compounds. The Coal Measures Clays (kaoline-rich) have the lowest sorption capacity, but also the lowest plasticity and have the most resistant clay minerals to alteration by leachate exposure.

1. INTRODUCTION

Leachates produced in municipal landfills constitute a health and environmental problem due to the different pollutants they content. For this reason, liners are required to minimise offsite migration of leachate. Two types of liners are currently used in modern landfills: synthetic liners, typically made of HDPE, and natural liners, typically made of compacted clay (Adar and Bilgili, 2015; Wei et al., 2018). Synthetic liners offer long-term impermeability to leachate but imply a high technology input and can be affected by slope stability, interface shear strength (Kavazanjian et al., 2006) and physico-chemical, thermal and mechanical problems (Kong et al., 2017), which may result in failure within 10 yrs of service (Rowe and Sangam, 2002; Rowe et al., 2003). Compacted clay liners are puncture-resistant and have advantageous reactive properties, but can be unstable in contact with leachate and susceptible to cracking under repeated wetting and drying cycles (Louati et al., 2018; Yesiller et al., 2000).

Because containment liners eventually fail independently of their low permeability properties, landfills are potential "ticking time bombs" that store and isolate waste until the confined pollutants are accidentally released to the environment in leachate. However, the intrinsic reactive properties of clays means they can biogeochemically interact with pollutants in leachates to decrease their availability and potential hazards over time. This reactivity (or attenuation) is enhanced if rainwater is allowed to enter the waste because then waste degradation is boosted, which accelerates its stabilization (Allen, 2001). The attenuation capacity of natural liners results in shorter periods of (1) potential release of pollutants and (2) aftercare monitoring, with subsequently lower landfill cost and less risk of environmental contamination. However, most attention has traditionally

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Detritus / Volume 12 - 2020 / pages 100-113
https://doi.org/10.31025/2611-4135/2020.13946

focused on the impermeability properties of liners as a performance characteristic. Here we focus on both impermeability and attenuation capacities, without relying solely on the impermeability (or containment) role, as a basis to improve liner design and performance. This dual capability can in principle be included in the engineering design of compacted clay liners to manage both organic and inorganic pollutants in leachate (Thornton et al., 1993; 1997).

The attenuation capacity, low cost and ease of implementation of compacted clay liners makes them more attractive than synthetic geomembranes on their own in landfill liner systems. This is particularly important in low-income countries where >90% of waste is openly dumped (Kaza et al., 2018), and in removing organic pollutants (Beaven et al., 2009). However, clays are very diverse in their physico-chemical properties and the suitability of the clayey substratum as a potential liner must be properly evaluated (Widomski et al., 2018). This task is complex and, in order to avoid any adverse effects, must consider the factors and the interactions between them, which affect leachate-liner system. There are many factors involved, such as liner mineralogy, shrink/swell potential, sorption capacity, dispersive/erosion behaviour and fluid permeability. If the clay plasticity is too high, construction of the liner becomes more difficult and the swelling/shrinking/cracking potential more significant as a failure mechanism.

In this study, the feasibility of four natural clayey substrata as landfill liners was evaluated. Their physico-chemical, mineralogical and geotechnical characteristics were studied and the results were discussed in terms of strengths and weaknesses as candidate materials for landfill liners. Finally, the potential for attenuation of pollutants in leachate by each material was evaluated for sustainable landfill applications. The aim was to characterise the relevant properties of the different clays in order to identify those which are geotechnical stable and effective in pollutant attenuation for liner design. This is essential to prevent pollution of the environment and protect human health from leachate spreading over groundwater aquifers or adjacent rivers and lands.

2. MATERIALS AND METHODS

2.1 Materials

Four clayey substrata from the United Kingdom were studied: London Clay (LC), Oxford Clay (OC), and shallow and deep Coal Measures Clays (SCMC and DCMC) (Table 1). The LC originated from shale, greensand, chalk, and lateritic soils during a sea level rise over the Northern Sea Basin. It is a silty to very silty clay, slightly calcareous with disseminated pyrite. The OC, collected from the Peterborough Member, contained many visible fossils (vertebrate and invertebrate), particularly bivalves (Meleagrinella). In contrast to the two previous clays, the Coal Measures Clays originated in a fluvio-deltaic environment and also have a relatively high proportion of iron sulphides (pyrite, marcasite) and gypsum, the latter following pyrite weathering. These Coal Measures Clays consist of interbedded clay, shales, silt and sand, interstratified with coal.

Approximately 100, 73, 25 and 20 kg of respectively LC, OC, SCMC and DCMC were recovered in-situ between June and July 2018. The pore water and cation exchange complex compositions were analysed in several subsamples before oven drying. The exchangeable cations were analysed in air-dried and powder samples (prepared with agate mortar and pestle) after applying 3 cycles of 10 sec of ultrasonification to a suspension of 0.15 mg clay in 50 mL deionized water. The elemental composition and mineralogy were determined after oven drying and grinding to a fine powder. For geotechnical tests the conglomerates were oven dried to remove residual moisture and the dry lumps broken up until a particle size <0.2 cm was achieved. For this, a rammer and several perforated screen trays fitted in a CONTROLS sieve shaker (Model 15 d040/a1) were used and the clays first reduced into approximately 2 cm aggregate lumps. Next, the <0.2 cm particles were recovered separately and the 0.2-2 cm lumps put into a bench soil grinder (Humboldt Co) and broken up to achieve <0.2 cm size. All results are expressed as a function of dry mass.

2.2 Analyses

The concentrations of nitrogen, carbon, hydrogen and sulphur were analysed in duplicate samples ground to ≤0.1 cm (0.005 g) using a Thermo Scientific FLASH 2000 Elemental Analyzer (CHNS). The remaining elements except oxygen and the halogens were analysed using a Spectro-Ciros-Vision radial ICP-OES instrument after acid digestion of 0.031 and 0.094 g at 150°C. For this, 12 mL of aqua regia was applied for 30 min followed by two 1 mL volumes of HF for 10 min, and the resulting solution was eluted up to 50 mL with 1 mass % HNO_3. The mineralogy was determined by X-ray diffraction (XRD) using a Ni-filtered Cu Kα radiation (k = 0.15406 nm) in a Philips X'Pert diffractometer,

TABLE 1: Information about the natural clayey substrata samples.

	London Clay (LC)	**Oxford Clay from Peterborough Member (OC)**	**Shallow Coal Measures Clay (SCMC)**	**Deep Coal Measures Clay (DCMC)**
Location (UK)	North Essex	Northwest Buckinghamshire	West Yorkshire, collected close to the surface	West Yorkshire, collected at a greater depth
Age	Eocene: 47.8 - 56.0 Ma	At the end of the Middle Jurassic: 164-166 Ma	Upper Carboniferous: 310 Ma	Upper Carboniferous: 310 Ma
Origin	Deep marine sediments	Deep marine sediments	Fluvio-deltaic sediments	Fluvio-deltaic sediments
Colour / appearance	Uniform, firm, brown colour	Grey colour with carbonaceous shells and rootlets	Dark grey-dark brown colour	Two-coloured: orange-light brown and dark brown
Selected references	Fannin 2006; Kemp and Wagner, 2006	Fannin 2006; Hudson and Martill, 1994; Scotney et al., 2012	Freeman, 1964, McEvoy et al., 2016	Freeman, 1964, McEvoy et al., 2016

operating at 40 kV and 40 mA, with a step size of 0.016 and a speed of 2 s/step. The samples were prepared by both sprayed random powder (after grinding down to 1-3 µm) and flat oriented slides (after obtaining the <2-µm fraction by dispersant and Stokes' law). Each oriented sample was prepared from a suspension of 0.1 g of the clay-fraction in 2 mL of a solution in three ways: (1) in water and air drying, (2) in water and 550°C drying for 2 h, and (3) in a glycerol solution and air drying (Moore and Reynolds, 1997). The software PDF-4+ 2019 (version 4.19.0.1) and the database v. 4.1903 were used for data interpretation. The content of organic matter, sulphides, hydroxyl groups and carbonates phases was determined by termogravimetrical analysis (TGA). Replicates between 0.015-0.030 g were heated from 30 to 995°C at a rate of 20°C/min with a TGA 4000 Perkin Elmer under two atmospheres: N_2 and O_2 gas (20 mL/min). The results were interpreted in combination with the CHNS, ICP-OES and XRD results. The external specific surface area was measured in 0.2-0.5 g of degassed material (60°C) by the Brunauer-Emmett-Teller (BET) method of nitrogen gas sorption at 77 K in both a Micromeritics Tristar II 3020 and Beckman Coulter SA-3100. The material was prepared from 1 g of original sample gently ground to <400 µm (at least 10 cycles) and discarding the fraction below 64 µm (Bertier et al., 2016). The particle size distribution as volume percent was determined by the Malvern Mastersizer 3000® (double) Laser Diffraction (software version 3.62) assuming the refractive index and density of silica SIO_2 (respectively 1.457 and 2.65 g/cm^3). Samples were dispersed in distilled water by stirring at 2500 rpm and ultrasonic treatment. Measurements of 10 min duration were repeated in the same sample until the results were constant and an average taken.

The pore water chemistry was obtained by mixing 20 mL of deionized water to 10 g of wet clay at room temperature. Sample pH was measured with a pH glass electrode in the water:clay mixture after settling for 24 h and shaking prior to the analysis. The solution was then centrifuged and filtered (0.45 µm) to measure the electrical conductivity with a 0.4-cm sensor, and the soluble elements. The soluble anions and cations were analysed by ion chromatography (Dionex ICS-3000), the alkalinity by titration with H_2SO_4 (HACH digital titrator) and the carbon soluble species using a TOC-V-CSH analyser (Shimadzu ASI-V). The cations in the exchange complex were determined as the difference between the cations extracted with a 1.26 M $SrCl_2$ solution (80 mL) minus the soluble fraction extracted with water (80 mL) after shaking with 5 g of clay for 10 minutes (Edmeades and Clinton, 1981). Due to the high ionic strength of the $SrCl_2$ solutions, sodium, potassium, calcium and magnesium in these extracts were analysed by atomic absorption spectroscopy, AAS (HITACHI Polarized Zeeman Z2300), whereas ammonium was analysed by atomic emission spectroscopy. $LaCl_3$ was added at 20% to standards and samples for the AAS analyses of calcium and magnesium. The cation-exchange capacity (CEC) was determined by copper complex with Cu-triethylenetetramine at pH 7-8, with a photometer at a wavelength for maximum extension of 579 nm (Holden et al., 2012; Stanjek and Künkel, 2016).

To study the consistency and engineering behaviour of the materials, the clay samples were hydrated with different amounts of water for 24 hours in sealed plastic bags prior to index property tests (Head, 2006). The consistency was studied in the <425-µm fraction (250 g) by the determination of two specific water (or moisture) contents: the liquid limit, LL (water content that separates the plastic and liquid states) and the plastic limit, PL (water content that separates the semi-solid and plastic states). The change of clay consistency from plastic to liquid state was determined by the free-falling cone test at a penetration of 2 cm into the wet sample, with duplicates differing ≤0.05 cm (BS 1377:2:4.3, 1990). The change of clay consistency from semi-solid to plastic state was determined by manual rolling wet samples (20 g) until threads of 0.3-cm diameter begin to crumble, with four replicates differing ≤2% moisture content of their PL (BS 1377:2:5.3, 1990 and ASTM D 4318, 2015). To know the range of water content in which the clayey material has a plastic consistency, the plasticity index (PI) was calculated as the difference between the LL and the PL (Head, 2006). All actual moisture contents were determined on a mass % dry basis (Equation 1) after oven drying 5-10 g of material (105°C, 48 h) with duplicates that differ ≤0.5%.

$$\mathrm{MC}(\%) = \frac{m_0 - m_d}{m_d} \times 100 = \frac{m_{0,c} - m_{d,c}}{m_{d,c} - m_c} \times 100 \qquad (1)$$

where MC is the moisture content dry basis (%), m_0 is the mass of wet sample before moisture removal (g), m_d is the mass of sample after drying (g), $m_{0,c}$ is the mass of wet sample plus container before moisture removal (g), $m_{d,c}$ is the mass of sample plus container after drying (g) and m_c is the mass of the container (g).

The optimal condition of the clays at which the susceptibility to settlement is reduced was studied by applying the same compactive effort in different hydrated samples (240-540 mL water in 1600-1800 g clays). The compaction was placed into a mould of 5.25 cm radius by 11.55 cm height, in three equal layers subjected to 27 blows each one, by a 2.5 kg rammer of 2.5-cm radius that dropped from a height of 30 cm (BS 1377:4:3.3, 1990). The optimum moisture content (OMC) was selected on the basis of the maximum dry (bulk) density (MDD) after the compaction. To calculate the particle density of the solids, the specific gravity (G_s) was obtained by triplicate tests at 20°C, in desiccated materials of <0.2 cm size (50 g) using air-dried pycnometers of 50 mL (BS 1377:2:8.3, 1990 but 20°C instead of 25°C). The porosity (n) was calculated as a percentage following Equation 2 (Equation 3 for the optimal conditions). The slight difference between n and void ratio (e) is that the latter measures the void volume (the sum of V_{air} and V_w) in relation to the volume of the solid instead of the total volume. Thus, e (normally expressed as a ratio) can be >1, but n cannot be higher than 100%.

$$n(\%) = \frac{V_{air} + V_w}{V_T} \times 100 = \frac{V_T - V_s}{V_T} \times 100 \qquad (2)$$

$$n_{opt}(\%) = \frac{V_T - \frac{m_{d,OMC}}{G_s}}{V_T} \times 100 \qquad (3)$$

where V_{air} is the volume of the air (mL), V_w is the volume of the water (mL), V_T is the total volume (mould of 1000 mL),

V_s is the volume of the solid particles (mL), $m_{d,OMC}$ is the dried mass of sample at the OMC (g) and Gs is the specific gravity (unitless).

Assuming that volumes of voids filled with air are constant ($\eta_{air,i}$), lines at different air void ($\eta_{air,1}$, $\eta_{air,2}$...) and saturation values can be drawn as a function of dry bulk density ($\gamma_{d,i}$) relative to the moisture content ratio (Equation 4). The difference between air void line (η_{air}) and saturation (s) is that the latter ratio measures the volume of water in relation to the void volume instead of the total volume. The zero-air void line ($\eta_{air} = 0$) corresponds to the maximum saturation ratio (s = 1).

$$\gamma_{d,i} = \frac{(1 - \eta_{air,i}) \cdot G_S \cdot \gamma_w}{1 + MCi \cdot G_S} \quad \text{being} \quad \eta_{air,i} = \frac{V_{air,i}}{V_T} \tag{4}$$

where $\gamma_{d,i}$ and MC_i are the dry bulk densities (g/cm^3) and the moisture contents (ratio) corresponding to the air void constant i, $\eta_{air,i}$ is the line corresponding to an air void and saturation constant i related to the total volume (ratio), G_s is the specific gravity (unitless) and γ_w is the density of water (1 g/cm^3).

The specific value for the air void and saturation line after compaction at the optimal conditions ($\eta_{air,opt}$) was calculated with the $\gamma_{d,i}$ and MC_i equal to MDD and OMC (ratio), respectively (Equation 5).

$$\eta_{air\ opt}(\%) = \left(1 - \frac{MDD\ (1 + OMC \cdot G_S)}{G_S \cdot \gamma_W}\right) \times 100 \tag{5}$$

The potential swell (S %) was determined based on its relationship with the Atterberg limits by the well-defined empirical Equation 6 (Seed et al., 1962):

$$\mathrm{S}(\%) = 216 \cdot 10^{-5} \cdot \mathrm{PI}^{2.44} \tag{6}$$

where PI is the plasticity index (%).

The hydraulic conductivity or permeability coefficient (K) was measured in aluminium permeation cylinders by centrifuging at 25 gravities (Regadío et al., 2020). Model liners were compacted into of 5 cm radius by 10 cm height cylinders after being hydrated with tap water at the OMC. Leachate from a municipal solid waste landfill and rainwater were used as permeating fluids. Rainwater was normally used for permeating model liners previously permeated with landfill leachate. Eleven cylinders on average were assembled per centrifuge test, each one connected to an intake line. All intake lines came from a common tank that provided continuous permeation to all the cylinders by applying a pressure of 1.1 bar. The tests were conducted under a 50% CO_2/N_2 anaerobic gas (for leachate permeation) or under compressed air (for rainwater permeation). The fluid head in the tank that provided the permeating fluid was measured every ≈2 days during 2.5 weeks under leachate permeation, or 4.5 weeks under rainwater permeation. The K measured in the centrifugal permeability tests ("experimental model") had a 25-fold enhanced gravity. To calculate the corresponding real value in the field (K "prototype"), the scaling law (Ng, 2014) was applied in the falling head equation for less permeable soils (Head, 1994) adapted to this method (Equation 7):

$$K = \frac{K_{exp.m} \cdot n}{n^2} = \frac{\frac{a\,L}{A\,t} \ln\left(\frac{h_0}{h_1}\right)}{n}, \text{being } h_1 = \frac{h_0 - (h_0 - h_{1\#})}{\#} \tag{7}$$

where $K_{exp.m}$ is the hydraulic conductivity in the experimental model (m/s), n is the enhanced gravity applied in the centrifugal experiment (25), a is the cross area of the tank (0.06158 m^2), L is the lengh of the liner specimen (0.10000 m), A is the cross area of the liner specimen (0.00785 m^2), t is the time period considered for the calculation (seconds), h is the head in the tank at the initial (if subscript 0) and final (if subscript 1#) points, # is the number of model liners connected to the tank.

3. RESULTS

3.1 Elemental composition and mineralogy

The four clayey substratum were mainly composed of silicium and aluminium, followed by iron, potassium, hydrogen and magnesium (Figure 1). This agreed with the expected high presence of clay minerals, potentially higher in Coal Measures Clays (see below). Silica, potassium, titanium, and especially magnesium were higher in the LC. The OC was notable for its high content in calcium, carbon, sulphur (g/kg) and strontium (mg/kg), with lower silica, iron and phosphorus content. The Coal Measures Clays were notable for their high concentration of aluminium, nitrogen and manganese, whereas the concentration of calcium, sodium, potassium, strontium and boron were the lowest within the four samples. In the case of SCMC, there was more carbon, nitrogen and sulphur than in DCMC. (Figure 1).

All samples contain smectite, illite, kaolinite and chlorite but in different proportions (Figure 2). Smectite was most important in LC, illite together with kaolinite in OC, and kaolinite (followed by illite) in the Coal Measures Clays. To a lesser extent, phlogopite mica was detected in LC, chlorite in both LC and OC, and interstratification (mixture of layers) of illite/smectite in OC and the two Coal Measures Clays.

Quartz and feldspars were the most important phases in all materials. These are accompanied by oxides except in the OC, which mainly contained calcium carbonate and iron sulphide (calcite and pyrite). Also relatively high levels of sulphides were found in SCMC, whereas, there were fluorides and oxide-fluoride in DCMC (Figure 3). The mass loss through heating due to dehydroxylation (associated with the mass of clay minerals) was the highest in the Coal Measures Clays (5-9%), while the highest mass loss due to decomposition of organics, sulphides and carbonates phases corresponded to OC (2, 4 and 5% respectively). Particulate organic matter as an associated material in these clays was especially high in the OC. It varied from 1.1 to 3.5% in the OC, in contrast to LC, SCMC and DCMC, which gave steady values of 1.7, 1.5 and 1.8%, respectively. The variability in the particulate organic matter content in the OC was due to its presence in many diverse forms: disseminated organic matter, coarse lignite fragments and fossils. Similarly, the carbonate phases in the OC varied from 4.5 to 6% due to the spread of carbonaceous shells.

3.2 Pore water and mineral surface characteristics

The LC had the highest natural moisture content followed by the OC (39 and 25 ± 2%, respectively), whereas SCMC and DCMC had the lowest values (10 and 12 ± 1%, respectively). This indicates a decreased water absorption and porosity from LC > OC > Coal Measures Clays. The pore water composition of the clayey materials of the OC was

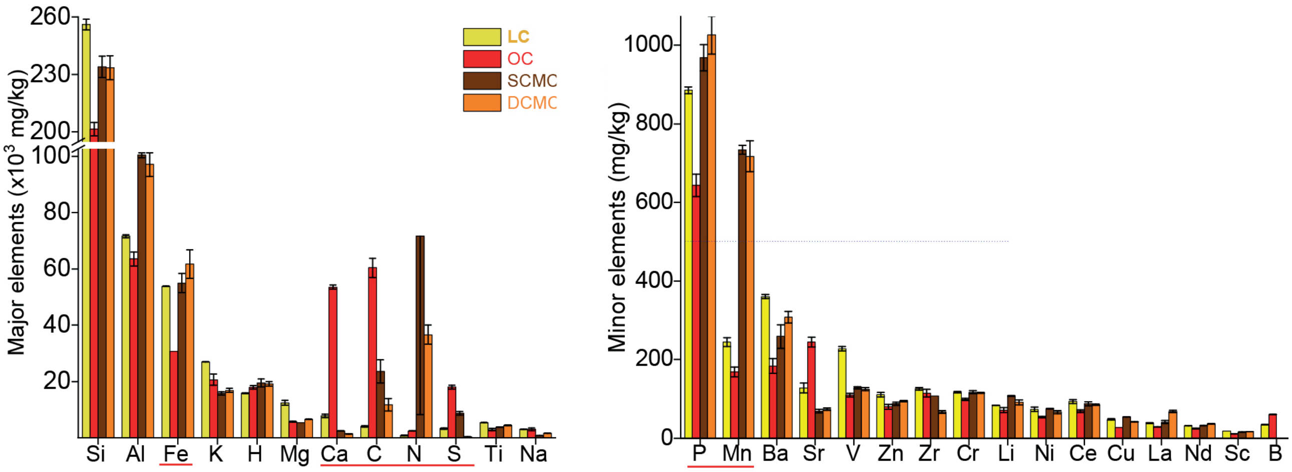

FIGURE 1: Elemental composition of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC).

the most basic due to the presence of calcium carbonate phases (pH 9.0) and the LC was close to neutral (pH 7.3). In contrast, the SCMC and DCMC were acidic (pH 3.8 and 5.4, respectively). Consistent with this, alkalinity was only present in the OC (10.3 mmol/kg as $CaCO_3$) and LC (1.7 mmol/kg as $CaCO_3$). The total dissolved ion content in terms of electrical conductivity in aqueous extracts (L/S 1:2.5) was between 1-3 mS/cm, except for DCMC (0.1 mS/cm) and for OC (5 mS/cm). The predominant soluble anion in all samples was sulphate (SO_4^{2-}), mainly balanced by calcium (Ca^{2+}) and sodium (Na^+) in both the LC and OC, by magnesium (Mg^{2+}) and Ca^{2+} in the SCMC and mostly Na^+ in the DCM. In all cases the concentration of potassium (K^+) was very low and ammonium (NH_4^+) was not detected. Only the OC had a significant content of soluble carbon in the pore water (10 mg/g).

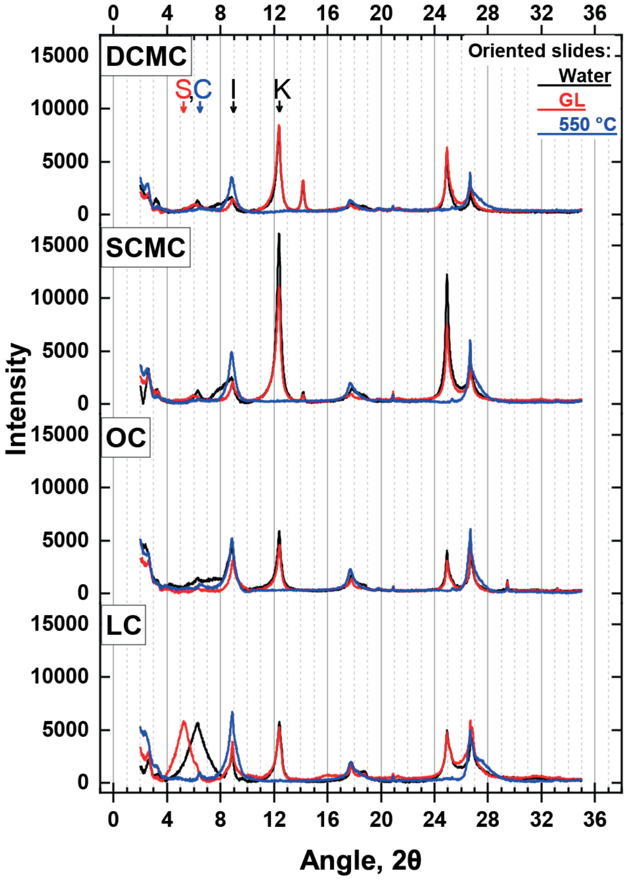

FIGURE 2: Sheet-silicate mineralogy of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). Water: water and air drying preparation, GL: glycerol and air drying preparation, 550°C: water and 550°C drying preparation. S: smectite d001 reflection under GL preparation, C (chlorite) and I (illite) d001 reflections under all three preparations. K: kaolinite d001 reflection under water and GL preparations.

As expected the exchangeable cations on the negatively charged sites of the clays and particulate organic matter were similar to the most abundant in the pore water. The sum of exchangeable cations often exceeded the total charge of the clay (CEC), due to high concentrations of Ca^{2+} released by dissolution of carbonate minerals. Thus, the CEC was measured directly instead of estimating this from the sum of exchangeable cations, to avoid bias from Ca^{2+}. The CEC at pH 7-8 decreased in the order: LC (26 cmol+/kg) > OC (16 cmol+/kg) > Coal Measures Clays (13 cmol+/kg). The external specific surface area increased in the order: LC < OC < DCMC < SCMC (9.3 ± 0.3, 12.8 ± 3. 6, 31.0 ± 1.0, 53.7 ± 1.0 m^2/g, respectively). The highest values corresponded to the material with the highest amount of hydrous aluminium phyllosilicates minerals (Coal Measures Clays), followed by the material with the highest amount of particulate organic matter (OC). Nonetheless, the total surface area (external plus internal) of the LC may be one of the largest due to its higher content of expandable clay minerals (illite + smectite) than non-expandable ones (kaolinite + chlorite).

3.3 Consistency classification and properties

The moisture contents at PL and LL were determined to identify clays susceptible to dispersion and excessive shrinkage in the field (Table 2). These parameters can distinguish between silt- and clay- size, and organic or inor-

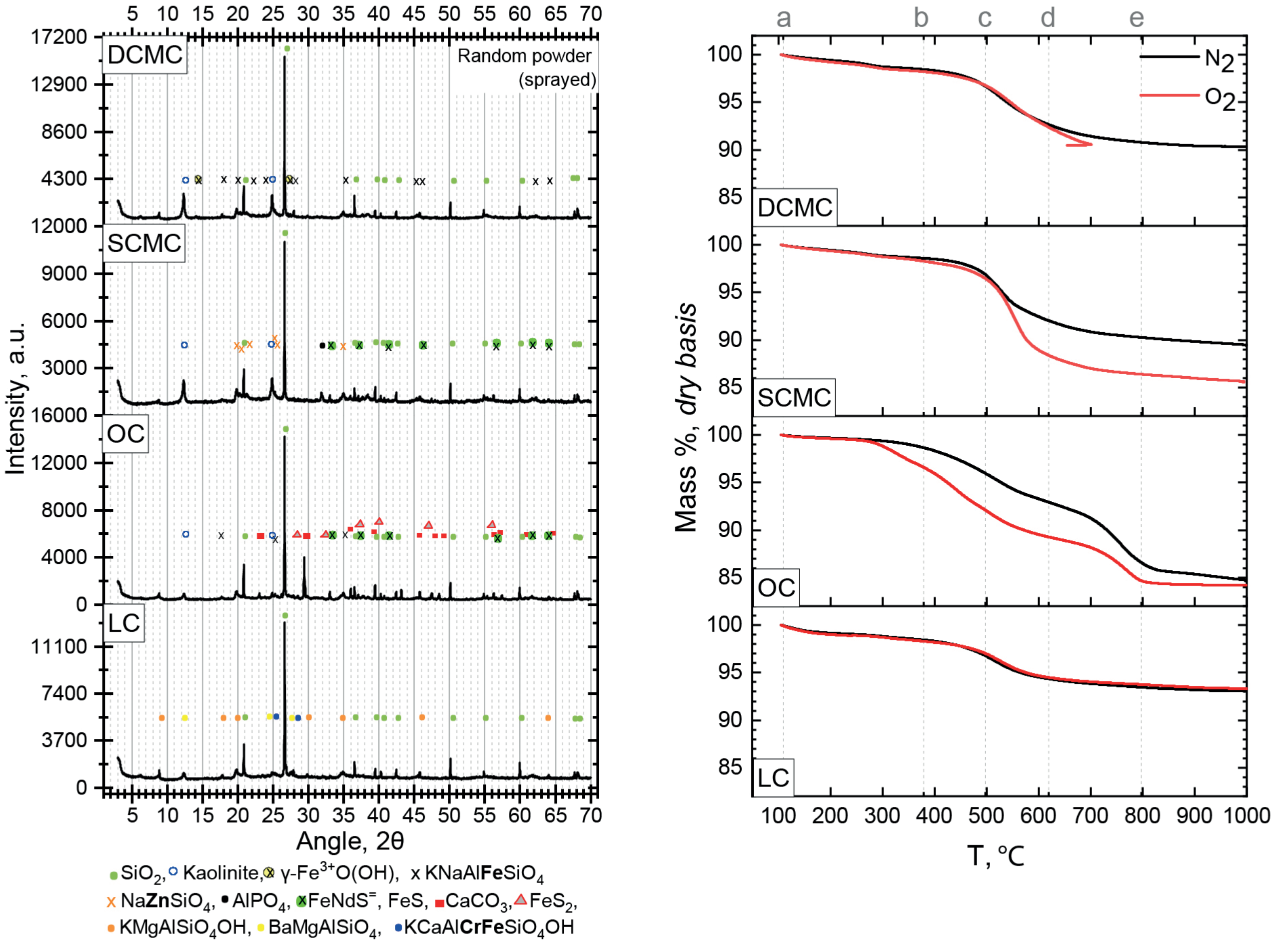

FIGURE 3: Left: Global mineralogy by sprayed random powder of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). Right: TGA curves with mass relative to the mass after dehydration (removal of interlayer water): (a-b) mass loss mainly due to thermal decomposition of organic matter, (b-c) mass loss due to thermal decomposition of sulphides, (c-d) mass loss due to dehydroxylation, (d-e) mass loss due to thermal decomposition of carbonate and (e-end) materials vitrification and formation of new phases (recrystallization).

ganic character. All clays had a LL >20%, confirming that they were cohesive materials. The LL and PI varied in the order: LC > OC > Coal Measures Clays, consistent with the dominant sheet silicate in each material: smectite, illite/kaolinite and kaolinite, respectively. The LC and OC had high plasticity, high toughness and high to very high dry strength (Figure 4). The high plasticity of LC was notable for the broad range of water contents at which this clay had plastic consistency (from 28 to 79%, i.e., PI = 51%), twice that of the OC. This is due to the presence of smectite (expandable clay mineral) and the higher content of clay-size particles in the LC compared with the other clays with a higher silt content. Ninety vol% of the LC was composed of particles ≤52 μm, whereas 90 vol% of the DCMC, SCMC and OC were made up of particles ≤130 μm, ≤136 μm and ≤185 μm, respectively. The two Coal Measures Clays gave similar results: intermediate plasticity, medium toughness and high dry strength. The potential to swell decreased from LC >> OC > SCMC > DCMC (30.2, 5.3, 2.6, 2.4%), as expected from the mineralogy and PI results. All studied materials had no dispersive clay fines as these do not occur in clays from intermediate to high plasticity with smectite. On the contrary, dispersive clays typically appear in soils classified as clayey of low plasticity (CL), sometimes also in silty and/or sandy soils with low plasticity (ML, CL-ML) (Figure 4).

The "A-line" on the plasticity chart (Figure 4) denotes the empirical boundary between inorganic materials and clays (above line) and organic clays and clastic silts (below line). The OC fell on the dividing line between inorganic and organic categories, while Coal Measures Clays and the LC fell above the line in the inorganic region, being the DCMC close to the organic silts, and the LC the most inorganic clay.

3.4 Compaction and permeability behaviours

Clays are normally compacted for placing and constructing the clay liners because to increase the shear strength and bearing capacity, which limits future settlement. In addition, the void ratio and permeability is decreased, and variations in volume change are less pronounced. Consequently, clays are less susceptible to cracking that would offer preferential flow paths for leachate leakage and groundwater seepage. To optimise this, clays should be compacted close to the OMC, the quantity of water nec-

TABLE 2: Moisture contents corresponding to the Atterberg consistency limits (<425-µm fraction).

	Linear regression		LL, %	PL, %		PI, %
	Slope	Intercept	Value (X when Y= 20)	Value	RSD, percent	Value
LC	0.552	-23.339	79	28	4.4	51
OC	1.136	-40.404	53	29	4.3	24
SCMC	1.758	-49.944	40	22	4.0	18
DCMC	1.368	-40.052	44	25	0.9	19

Linear regression: relationship of the cone penetration (Y-axis in mm, as a reverse measure of the shear strength) on the moisture content (X-axis in %), LL (or WL): liquid limit, PL (or WP): plastic limit, PI (or Pi): Plasticity index, RSD: relative standard deviation (the standard deviation divided by the average and multiplied by 100), LC: London Clay, OC: Oxford Clay, SCMC: shallow Coal Measures Clay, DCMC: deep Coal Measures Clay.

essary to achieve the maximum dry (bulk) density. Under the same compaction effort, the OMC followed the order LC > OC > Coal Measures Clays, while the maximum dry (bulk) densities followed the inverse sequence (Figure 5). The clay sequence for OMC agreed with those for air void lines and for porosity (both after compaction at the optimal conditions), and with the higher plasticity of LC, followed by OC, which could accommodate more water to achieve their maximum dry densities than the Coal Measures Clays. The particle density of the solids, in terms of specific gravity, followed the order LC > Coal Measures Clays > OC due to the higher particulate organic matter content of the last one (Figure 5). Both Coal Measures Clays had very similar consistency and engineering behaviour (Figure 4 and Figure 5).

The K for leachate and rainwater through the most plastic clays (LC and OC) amended with sandy materials was measured over time. In all three tests run with landfill leachate, K slightly increased from initial values of 0.1 and $0.3\cdot10^{-9}$ m/s to a maximum of 0.6 and $0.8\cdot10^{-9}$ m/s after an initial time equivalent to 8-15 yrs. Then, K decreased to comparable values at the start (Figure 6). Only on three separate occasions during leachate permeation through liners of 20% sand, K exceeded the maximum legal limit: in the beginning (between 0 and 3.1 yrs), in the middle (between 8.2 and 10 yrs) and towards the end (between 25.4-27.1 yrs). However, the average of K measurements taken in 9 different periods over a total modelled time equivalent to 32 yrs prototype of leachate through the liners of 20% sand was $0.8\cdot10^{-9}$ m/s (± $0.6\cdot10^{-9}$), and lower through the liners of 10% sand ($0.3\cdot10^{-9}$ m/s (± $0.2\cdot10^{-9}$)). When changing to rainwater though liners of ≈6% sand, there was also in the beginning a slight increase of K with time up to $0.5\cdot10^{-9}$ m/s, followed by a decrease with a stabilization around $0.2\cdot10^{-9}$ m/s (±$0.1\cdot10^{-9}$) from year 44 onwards (30 yrs of leachate permeation followed by 14 yrs of rainwater, Figure 6). The average of K for rainwater permeation taken over 16 periods of time within the total time modelled (53 yrs prototype) was $0.3\cdot10^{-9}$ m/s (±$0.1\cdot10^{-9}$) though the liners of ≈6% sand. The accumulated K calculated as a single measurement over the entire test time (≈19 days each test) was very close to the average K calculated with all intermediate measurements taken every ≈2.3 days over the 19-day tests (Table 3). This together with the small standard deviations of the K in liners with 10% or less sand, denotes that their K variation describe above was not very significant.

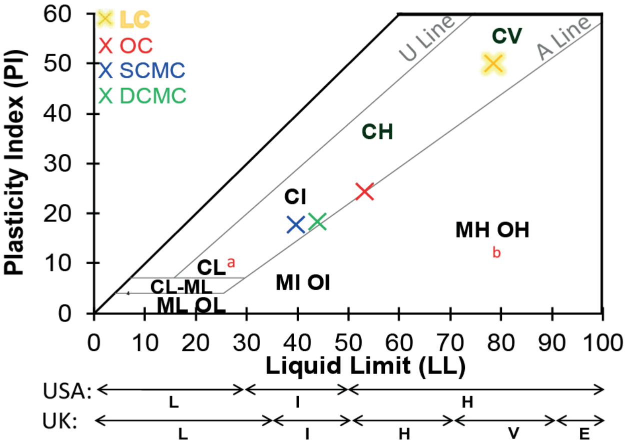

FIGURE 4: Plasticity chart for soil classification (<425-µm fraction) of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). Divisions of plasticity in: L: low, I: intermediate, H: high, V: very high and E: extremely high, according to USA and UK. O: significant organic material; C: clayey; M: silty and/or sandy (Unified Soil Classification System, USCS). [a] dispersive clay fines, [b] non dispersive clay fines. U-line: upper reference bound of PI for natural soils defined by two equations: PI = 7 if LLs ≤16, and PI = 0.9 (LL- 8) if LLs >16. A-line: reference boundary of PI between the clay soils (above line, mostly inorganic) and the silt soils (below it) defined also by two equations: PI = 4 if LLs ≤25.5, and PI = 0.73 (LL- 20) if LLs >25.5 (Casagrande, 1947).

4. DISCUSSION

Based on the previous analysis, the feasibility of the four natural clayey substrata to attenuate landfill leachate is discussed below. Although its composition varies, landfill leachate always contains high concentrations of Na^+, K^+, bicarbonate and chloride, with significant NH_4^+ and organic compounds. The heavy metal content is generally relatively low, often of no major concern and limited to chromium, nickel and zinc (Aucott, 2006; Kjeldsen et al., 2002). As NH_4^+ and K^+ are major elements in landfill leachate and virtually absent in these Ca-clay mineral liners, both can be used as tracers in leachate migration studies. The differences between the clayey substrata on porosity, density, sorption, surface, plasticity, permeability are due to their origin, particle size and mineralogy (Table 1 and from Figure 1 to 3). The presence of carbonaceous material is characteristic of clays formed in alluvial or shallow waters, as is the case with Coal Measures Clays (Bain, 1971). Smectite is often found interstratified with illite and in mixtures with chlori-

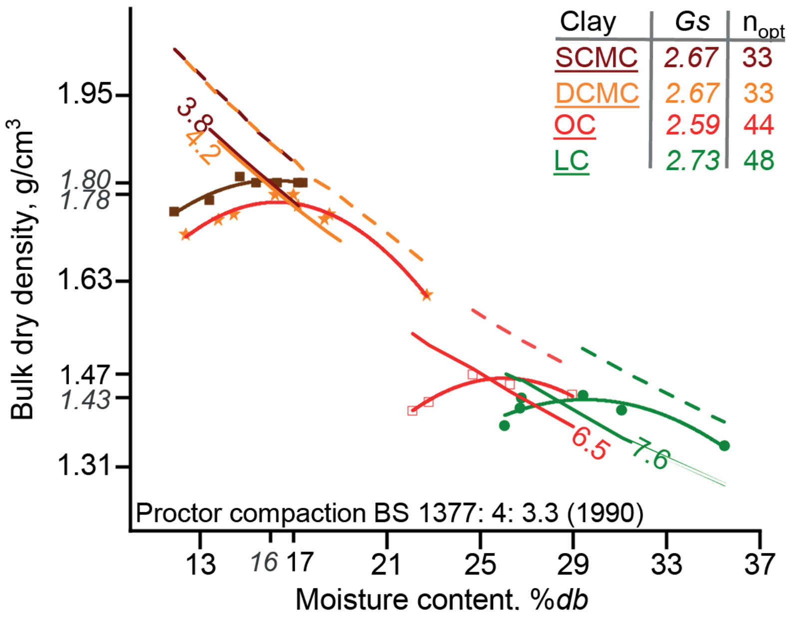

FIGURE 5: Air void lines (air vol% of the total volume) and compaction curves under Proctor BS 1377:4:3.3 (1990) to estimate the (optimum) moisture contents at which the dry bulk densities are maximum. Dashed straights: zero air line or full (water) saturation lines (s=1). Solid straights: air void lines at the optimum. n_{opt}: porosities at the optimum (air plus water vol% of the total volume). Gs: specific gravity (unitless). LC: London Clay, OC: Oxford Clay, SCMC: shallow Coal Measures Clay and DCMC: deep Coal Measures Clay.

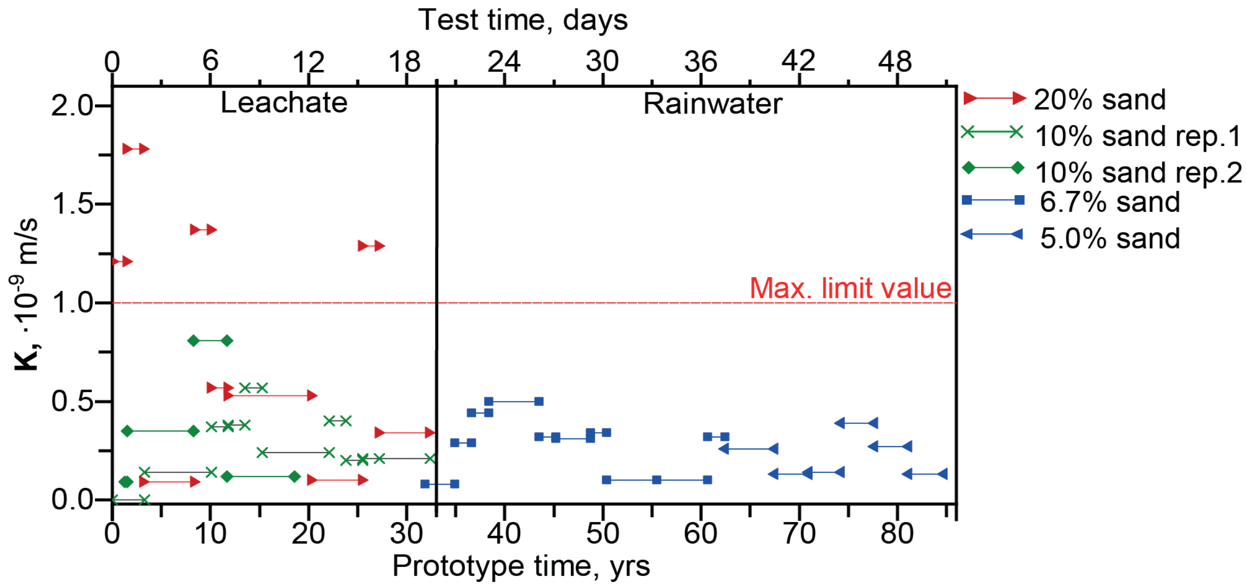

FIGURE 6: Hydraulic conductivities (K) of landfill leachate (from year 0 to 33) and rainwater (from year 33 to 82) through model liners (≈11) of averaged compositions made of clays and mixtures of clays with sandy non-cohesive materials. The mixtures were used to decrease the plasticity of London and Oxford clays and therefore its associated risk of shrinkage.

te and sometimes kaolinite in deep sea marine sediments, as for the LC and OC. A high silica-to-aluminium ratio is characteristic of clays with smectite minerals (Weaver and Pollard, 1973), agreeing with that the LC had the highest values of this ratio and of smectite.

4.1 Evaluation as attenuation liners

In addition to the low permeability that they provide, compacted clays can attenuate leachate pollutants by sorption, dilution, redox transformations, biodegradation, precipitation and filtration (Allen, 2001; Griffin et al., 1976; Thornton et al., 1993). Attenuation here refers to a reduction of the mass of pollutants by naturally-occurring processes (Regadío et al., 2015). These attenuation processes occur simultaneously and can affect more than one pollutant in leachate. By sorption, pollutants are attached to mineral phases or particulate organic matter by a physical or chemical process, which encompasses ion exchange, adsorption, absorption and chemisorption. By redox transformations, organic and metal compounds are converted

TABLE 3: Hydraulic conductivities in m/s (K) as a single accumulated measurement within the entire test and as an average of the intermediate measurements taken every 2-3 days throughout the test.

Average liner composition	Permeating test time	Permeating fluid	One accumulated measurement	Average (± standard deviation) of intermediate measurements
Clays with 20% sand	From day 1 to 19	Landfill leachate	$0.45 \cdot 10^{-9}$	$0.81 \cdot 10^{-9}$ ($\pm 0.61 \cdot 10^{-9}$)
Clays with 10% sand (1)	From day 1 to 19	Landfill leachate	$0.21 \cdot 10^{-9}$	$0.25 \cdot 10^{-9}$ ($\pm 0.17 \cdot 10^{-9}$)
Clays with 10% sand (2)	From day 1 to 19	Landfill leachate	$0.29 \cdot 10^{-9}$	$0.27 \cdot 10^{-9}$ ($\pm 0.33 \cdot 10^{-9}$)
Clays with 6.7% sand	From day 19 to 36	Rainwater	$0.25 \cdot 10^{-9}$	$0.28 \cdot 10^{-9}$ ($\pm 0.14 \cdot 10^{-9}$)
Clays with 5.0% sand	From day 36 to 48	Rainwater	$0.22 \cdot 10^{-9}$	$0.22 \cdot 10^{-9}$ ($\pm 0.11 \cdot 10^{-9}$)

(1) and (2) are replicates.

into less toxic or immobile forms by electron transfer reactions. By biodegradation, organic pollutants are chemically decomposed by microorganisms. By precipitation, metallic pollutants become less bioavailable or mobile. By filtration, larger pollutants such as metal-organo complexes in the leachate remain physically trapped within the liner fabric.

The surface of soil particles is critical for the chemical reactions, sorption, colloid filtration, and transport of contaminants. All clayey materials and especially the OC contained particulate organic matter (Table 1, Figure 3 right, Figure 4) which has a large surface area and CEC. Particulate organic matter is important for the attenuation of contaminant molecules by sorbing them to its surface or fostering microbial communities that would breakdown the contaminants to less toxic or nontoxic compounds (see biodegradation below). The CEC in particulate organic matter and also in clay minerals is especially important for sorption. In this case cations in the pore water are sorbed by clays to neutralize their negative charge created by unbalanced substitutions of their structural cations. Sorbed native cations can be replaced by cationic pollutants in the leachate. Illites (present in the four clays here) have high affinity for selective sorption of NH_4^+ and K^+ due to their size compatibility with the interlayer (exchange) sites in this clay lattice (Griffin et al., 1976). Smectites (in the LC) also fix these cations but this destabilizes smectitic minerals, resulting in illitization, i.e., partial collapse of smectites with their subsequent conversion into illite. In the case of larger cations, organic cations or organometallic complexes in leachate, smectites sorbed these species preferentially relative to smaller, inorganic or uncomplexed metals (Koutsopoulou and Kornaros, 2010). This is because for the same valence these weakly hydrated cations are the easiest to sorb in the exchange sites than stronger hydrated small cations (Teppen and Miller, 2006), and only smectites have an exchanger interlayer space large enough to accommodate them. Smectite, along with vermiculite (interlayer Mg), has a high CEC, while illite has mid-range values and kaolinite very low values. Thus, the capacity to reduce the concentration of cationic pollutants in leachate by cation exchange reactions follows the order LC > OC > Coal Measures Clays. CEC generally increases with pH due to the development of greater negative charge (average pH in leachate is 7-8).

Anion sorption (bicarbonate, chloride, sulphate from leachate) is less efficient and very similar for the different clay minerals (kaolinite, smectite). It occurs at OH^- ions exposed on the mineral edges and is enhanced by positively charged iron-oxide colloids (present in LC and Coal Measures Clays) associated with clays (Raymahashay, 1987). Bicarbonate is the major inorganic anionic compound in leachate and largely determines the acid-base neutralisation potential of the system. This is good for Coal Measures Clays which have no pH buffering capacity to attenuate acidic episodes caused for example by oxidation of sulphides (pyrite) by infiltrating rainwater (Thornton et al., 2001). This oxygenated water can re-oxidized sulphide phases, resulting in the release of previously attenuated metals that precipitated earlier in such immobile phases (Regadío et al., 2013). Bicarbonates in the leachate itself would provide acid neutralization capacity to Coal Measure Clays which lack calcite. The acidity in Coal Measures Clays most likely arises from oxidation of pyrite in the upper, weathered zone, which produces a low pH, gypsum and amorphous iron oxides as by-products. Chloride is not significantly attenuated and mainly diffuses through the clay liner, together with Na^+ and the cations displaced from the exchange sites of clays (usually Ca^{2+} and Mg^{2+} substituted by NH_4^+, K^+) (Regadío et al., 2012; Zhan et al., 2014). These elements are diluted by the receiving groundwater and are generally not a problem due to its low toxicity even at relatively high concentrations. Sulphate in leachate is attenuated by anaerobic microbial reduction, a common redox process in landfills (Batchelder et al., 1998). All the studied clayey substrata contain redox-sensitive species, the most important being pyrite in the OC and SCMC, and iron oxides in the LC, SCMC and DCMC. As a result, these clays support the metals to precipitate as sulphides in the liner and the sulphate is in low concentration in leachate.

Biodegradation is also accompanied by changes in redox potential in the landfill, which results in transformation of organic and inorganic species by reactions under aerobic and a range of anaerobic conditions. Depending on the specific redox conditions in the landfill and liner (aerobic, nitrate-reducing, iron-reducing, sulphate-reducing, etc.), one or other organic compounds can be biodegraded (Bright et al., 2000). The concentration of the oxidising agents and their reduced species in the leachate indicates the redox conditions (Taylor and Allen, 2006). Differences in clay minerals have a minor effect on the biodegradation of organic pollutants than on the sorption of inorganic pollutants. This is because organic pollutants are attenuated mainly by anaerobic biodegradation (Thornton et al., 2000; Bright et al., 2000; Adar and Bilgili, 2015), rather than by sorption to clay minerals, in which case only smectite, chlorite and vermiculite would show significant organic sorption (Koutsopoulou and Kornaros, 2010). The decomposition of organic compounds down to water, methane and carbon dioxide, depends on the establishment of an appropriate microbial population. The native particulate organic matter of clay materials is essential to support in situ biological activity in liners, with the highest organic matter content found in the OC (followed by SCMC), sampled from a fossiliferous location (Martill et al., 1994). Anaerobic degradation in the liner is also sustained by the microbial inoculum in the leachate itself.

The attenuation of heavy metals in leachate is associated with particulate organic matter and mineral phases, including clay minerals in liners, and occurs by a combination of sorption, redox transformation and precipitation processes (Fannin, 2006). These processes are supported by specific mineral phases such as sulphate-bearing species (pyrite, gypsum), iron and manganese oxides and oxyhydroxides, and clays (mainly smectite and illite) (Fisher and Hudson, 1987). The studied materials all contain a high content of clay minerals which assists retention of heavy metals. The OC and SCMC contain pyrite, and the LC, SCMC and DCMC contain iron/metal oxides. The high native particulate organic matter content of the OC favours sorption of metals, whereas the dissolved organic compounds in leachate favour the formation of soluble metal-organo complexes. Despite the fact that metal-organo complexes are dissolved in leachate and therefore mobile, they can be attenuated by filtration due to their larger size (Christensen et al., 1996; Gregson et al., 2008). However, a proportion of metals complexed with dissolved organic matter or associated with colloids in leachate may not be attenuated (Thornton et al., 2001).

4.2 Evaluation as containment liners

None of the clays here were identified susceptible to dispersion in the field. Dispersive clays resemble normal clays but can be highly erosive and susceptible to severe damage or failure. Soils of high plasticity silt (MH in the USCS classification, Figure 4) and smetite-rich materials (LC) rarely contain dispersive clays. In the case of the LC, smectites are responsible for the adhesion forces between particles, which helps to prevent dispersion and thus soil erosion. The locations of the clays on or above the "A-line" on the plasticity chart (Figure 4), denotes a relatively low silt content so they are easy to compact well, resulting in low erodibility. The high OMCs of the OC and LC (25-29% with maximum dry bulk densities of 1.43-1.47 g/cm^3), indicate the abundance of clay-sized particles (heavy clays) as silt-rich soils have medium values and sandy materials have very low values. Coal Measures Clays had 16-17% of OMC with maximum dry bulk densities of 1.78-1.80 g/cm^3, being more characteristics of sandy-clay materials. In the case of shrinkage potential, only LC presented high risk because of the smectites. Concordantly, the LC was classified as high shrinkage (average shrink limits of 16.8±4.8%) compared to the OC as medium shrinkage (14.5 ±2.0%) in Hobbs et al. (2019). In addition, smectites can also sorb larger quantities of water that decrease the soil strength, causing destructive landslides and slope failure (Borchardt, 1977; Wagner, 2013; Yalcin, 2007). To ensure landfill liner stability, clays should have PIs of 15-30% (25% is good) and clays with PI >40% should not be used on their own.

The LC and OC are plastic clays and thus contain little sand and much clay, with a particular abundance of swelling minerals (illite and smectite). These are expandable sheet silicates with desirable properties such as erosion resistance, low permeability and excellent ability to attenuate pollutants, due to high surface area and CEC (e.g., the LC). Thus, they have been used globally to improve compacted soil liners (Ruiz et al., 2012) and to achieve permeabilities in geosynthetic clay liners in the low range of $0.10 \cdot 10^{-9}$-$0.01 \cdot 10^{-9}$ m/s (Egloffstein, 2001). A key limitation is that smectites are plastic minerals very sensitive to the cation occupying the hydrated interlayer, which results in a high potential for swelling or shrinkage in water or leachate, respectively. This property can induce instability and cracks in compacted clays and increase leakage through liners (Borchardt, 1977; Wagner, 2013; Yalcin, 2007). This risk can be reduced by compaction and by addition of sand (Tanit and Arrykul, 2005; Varghese and Anjana, 2015). No consensus exists though on whether applying a water content lower (Widomski et al., 2018) or higher (Benson et al., 1999) than the optimum, will limit the shrink potential and thus desiccation cracking, ensuring K values $\leq 1 \cdot 10^{-9}$ m/s. A further drawback of smectites is that their alteration to newly formed illite or even kaolinite results in much less chemo-mechanical stable materials than kaolinite-rich and illite-rich samples that are not originally derived from smectite (Zhao et al., 2007). This illitization at the expense of the smectite content can occur after ammonium and potassium sorption from the landfill leachate (Regadío et al., 2015), reducing the CEC of the clay by ≤10%.

The Coal Measures Clays were easily compacted until negligible air was present in their voids (4%), which is convenient to achieve a low permeability in the liner. The OC and LC can achieve the lowest K (Maritsa et al., 2016) due to their high plasticity, but also have a higher shrinkage risk, with consequent risk of increased K due to desiccation cracks. This is especially critical in the LC as its PI is >30%: the low K of compacted clay liners with such high plasticity could increase above the design specification after repeated cycles of shrinkage-by-drying and swelling-by-wetting, and never recover its initial value even after rewetting (Widomski et al., 2018). Conversely, low plasticity clays have a K that remains nearly constant and within the design specification, even after several drying/wetting cycles. Another advantage is that non-plastic clays exhibit predominant vertical instead of horizontal deformation, the latter being predominant in plastic clays. Vertical deformation presents a lower risk of desiccation cracking in a compacted clay liner. Thus, for the centrifuge permeability tests the sandy materials were added to both clays to decrease their plasticity (Mansouri et al., 2013; Tanit and Arrykul, 2005; Varghese and Anjana, 2015).

Adding non-cohesive materials decreases the LL and swell index, but should be done with caution to avoid an excessive increase in K (Lee et al., 2005). The K varies depending on the solid properties (surface area, particle sizes, porosity, tortuosity…), and many factors such as:

- Lab or field measurements (Allen, 2000; Benson et al., 1999; Shackelford and Javed, 1991);
- Compaction (Herrmann et al., 2009);
- (liquid) saturation ratio (Benson et al., 1999; Widomski et al., 2018);
- Other minor construction variables (Benson et al., 1999);
- Permeating liquid (di Emidio et al., 2017; Francisca and Glatstein, 2010; Jo et al., 2001; Lee et al., 2005; Singh and Prasad, 2007; Stepniewski et al., 2011; Uma Shankar and Muthukumar, 2017);
- Methodology (Sandoval et al., 2017);
- Passing of time and wet-dry seasonal variations (di Emidio et al., 2017; Egloffstein, 2001; Mitchell and Jaber, 1990; Stepniewski et al., 2011; Widomski et al., 2016).

The low K measurements ($0.2\text{-}0.8 \cdot 10^{-9}$ m/s) showed that these clayey substrates are chemically compatible with landfill leachates and promising candidates for use in the design of landfill bottom liners to minimize leachate migration as dual impermeability-attenuation barriers. The K values in the clay liners with ≤10% sandy materials under long-term leachate and rainwater permeation were below the most common maximum regulatory criterion ($1 \cdot 10^{-9}$ m/s) over a time equivalent to 85 yrs. These experimental results are in line with the graphical and multivariate regression of Benson et al. (1994), which estimates K values of $<1 \cdot 10^{-9}$ m/s for materials with at least 20% LL, 7% PI, 30% fines and 15% clays. No significant differences were found between the K values measured between different periods of time. The little variation is most likely due to the not complete (but almost) saturation of the compacted liners at the beginning (Darcy, 1856). This results in measurements of unsaturated K whose values are typically lower than those of saturated K as the water would be strongly attracted by the tension of the dry soil. The possible loss of the hydraulic connection when the pore water at the bottom of the model liner is transferred to the collector during spinning would also promote unsaturated conditions with lower K. Additionally, there are other processes that can also be affecting K. The leachate, with a high concentration and valence of ions, would decrease the net particle charge (Chorom and Rengasamy, 1995) and thickness of the Diffuse Double Layer (di Emidio et al., 2017; Schmitz, 2006; Stepniewski et al., 2011) in an initial stage. The former is due to the decrease in the dispersion of clays and the latter is relevant for the high porosity of freshly compacted soils. For Ca-clay minerals like here, the maximum dispersion occurs at pH 6.5-7.7 (Chorom and Rengasamy, 1995), which is the pH for most leachates. As a result, the transport of charged species in clays with high plasticity is enhanced, resulting in an increase of K in the first years. This supports earlier observations of an increase of K with the leachate concentration (Mitchell and Soga, 2005). In a later stage the precipitation of mineral phases and the growth of microbial activity may contribute to pore clogging (Francisca and Glatstein, 2010; Stepniewski et al., 2011) and therefore the decrease of K after its maximum during the previous stage (Figure 6). Calcite is likely to precipitate within the liner due to the basic pH, the high leachate bicarbonate concentration and additional dissolved calcium released over time by cation exchange reactions with the liner (de Soto et al., 2012; Thornton et al., 2001).

5. CONCLUSIONS

The performance of four natural clayey substrata as potential landfill liners was assessed by measuring their physico-chemical properties and stability and alterability upon contact with leachate, followed by rainwater. The attenuation of pollutants in leachate depends on the pollutant species and liner mineralogy. Potassium, ammonium, (dissolved) organic compounds and heavy metals (chromium, nickel and zinc) are the most representative leachate pollutants, according to their concentration, toxicity or persistence. All studied clayey materials are useful for the attenuation of leachate pollutants in sustainable waste landfills. These pollutants are mainly attenuated in the clayey materials by anaerobic biodegradation and sorption mechanisms, especially cation exchange. Chloride and sodium in leachate and native cations released from exchange sites on the clay liner after sorption of pollutants can be diluted by groundwater. However, different management options should be applied depending on the clayey material. The LC is the best material based on the sorption capacity and erosion resistance. However, the LC has a large plasticity (high susceptibility to excessive shrinkage) and easily alterable smectite clay minerals that partially collapse to illitic structures. Illitization has less impact on the CEC of the liner than on its chemo-mechanical stability and could be countered by compacting and mixing LC with sands. The OC is also plastic but to a lesser extent, with an acceptable PI. This substratum has a significant sorption capacity and is the best material for buffering acid leachates (due to native calcite) and supporting biodegradation of organic compounds. On the negative side, Coal Measures Clays have the lowest sorption capacity and zero neutralization power. However, they have the lowest plasticity and the most resistant clay minerals (kaolinite accompanied by illite) to alteration by exposure to leachate. In addition, both Coal Measures Clays are easily compacted until negligible air voids, which favours the achievement of a low K. The SCMC contained sulphate-bearing species (resulting from oxidation of pyrite) that enhance the retention by precipitation of heavy metals through bacterial sulphate reduction in the liner. The DCMC had very low mineral phases or inorganic salts that are readily dissolved in water. This is advantageous as it results in less mobilization of leachable salts from the liner itself. The LC and Coal Measures Clays have associated iron/metal oxides and oxyhydroxides that can enhance anion exchange and the removal of metals by sorption. Redox-sensitive species such as pyrite (OC and SCMC) and iron oxides (LC and Coal Measures Clays) can enhance the removal of metals by bacterially-mediated redox transformation and precipitation processes. The presence of pyrite and iron oxides also determines to a large extent the acid-base neutralisation potential, together with native carbonates in OC and bicarbonates in the leachate. After permeation with landfill leachate and rainwater during several weeks (equivalent to years under field conditions), the model liners achieved long-term sustainable low K, that rarely surpassed the maximum value specified for liner design.

ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 743880. This work reflects only the author's view, exempting the community from any liability. The authors thank TerraConsult Ltd and Soil Hill Quarries Ltd for providing the clay materials; technicians of the Dept of Civil and Structural Engineering and Dept of Chemical and Biological Engineering for general support (The University of Sheffield), J Cuevas and A Ortega for XRD analyses (Autonomous University of Madrid); the German-Austrian-Swiss Clay Group (DTTG), Craig Fannin (TerraConsult Ldt) and the Solid Waste Institute for Sustainability (SWIS) for insightful discussions.

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