THE ROLE OF NATURAL CLAYS IN THE SUSTAINABILITY OF LANDFILL LINERS

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ABSTRACT: Engineered synthetic liners on their own are not the ideal solution to protect land, water and living beings against landfill leachate pollution. Despite their impermeability, engineered liners are susceptible to fail during installation and after a few years of landfill operation, and have no attenuation properties. Conversely, natural clay liners can attenuate leachate pollutants by reactions of sorption, dilution, redox, biodegradation, precipitation and filtration; resulting in a decrease of the pollution load over time. Depending on the clay, significant differences exist in the shrinkage potential, sorption capacity, erosion resistance and permeability to fluids; which would affect the suitability and performance of the potential clay liner. Here, the physical, chemical, mineralogical and geotechnical characteristics of four natural clayey substrata were compared to discuss their feasibility as landfill liners. All the studied clayey substrata had favourable properties for 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 easily alterable clay minerals that partially collapse to illitic structures. Oxford clay (illite rich) is the best material for buffering acid leachates and degrading organic compounds. The Coal Measures Clays (kaoline-rich) have the lowest sorption capacity, but on the plus side they have the lowest plasticity and most resistant clay minerals to alteration by leachate exposure.

Keywords: compacted clays, attenuation, landfill liners, leachate pollutants

AKNOWLEDGEMENTS

1. INTRODUCTION

Leachates produced in municipal landfills constitute a health and environmental problem due to the different pollutants present in these liquors. 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, imply high technology and can be prone to failure within 10 years of service (Rowe and Sangam, 2002). Compacted clay liners are puncture-resistant and natural materials, but can be unstable and susceptible to cracking under repeated wetting and drying cycles (Louati et al., 2018; Yesiller et al., 2000). Interestingly, clays have intrinsic reactivity properties which means they can biogeochemically interact with pollutants in leachates to decrease their availability and potential hazards over time. This reactivity is enhanced if rainwater is allowed to enter the waste, because then waste degradation would be boosted, which would accelerate its stabilization (Allen, 2001). This results in shorter periods (1) of risk of contamination and (2) of aftercare monitoring and, subsequently, lower landfill cost.

The low cost, ease of implementation and reactivity 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). However, clays are very diverse and the suitability of the clayey substratum as a potential liner must be properly evaluated. This task is complex and, in order to avoid any adverse effects, must consider many factors with their interactions such as: (1) mineralogy, (2) shrink/swell potential, (3) sorption capacity, (4) dispersive/erosion behaviour and (5) permeability to fluids. 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 waste 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), 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 well-preserved fossils (vertebrate and invertebrate), particularly bivalves (*Meleagrinella*). In contrast to the two previous clays, the Coal Measures Clays originated in fluvio-deltaic environments and thus, 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.

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

Approximately 100, 73, 25 and 20 kg of LC, OC, SCMC and DCMC were recovered in-situ between June and July 2018. The pore water and exchange complex compositions were analysed in several subsamples that were not dried in the oven. The exchangeable cations were analysed from air-dried and powder samples (agate mortar and pestle) after applying 3 cycles of 10 sec of ultrasonification. 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 <2 mm. For that, with a rammer and several perforated screen trays fitted in a CONTROLS sieve shaker (Model 15 d040/a1), the clays were first reduced up to maximum 20 mm aggregate lumps. Next, the <2 mm particles were recovered separately and the 2 to 20 mm lumps were discharged into a bench soil grinder (Humboldt Co) and broken up to <2 mm size. All results are expressed on a dry mass basis.

2.2 Analyses

The concentrations of nitrogen, carbon, hydrogen and sulphur were analysed in duplicate samples ground to ≤1 mm (0.005 g) using a Thermo Scientific FLASH 2000 Elemental Analyzer. The remaining elements except oxygen and the halogens, were analysed using a Spectro-Ciros-Vision radial ICP-OES instrument after acid digestions of 0.031 and 0.094 g at 150 °C. For that, 12 mL of aqua regia was applied for 30 min and, twice 1 mL of HF for 10 min, and the resulting solution was eluted upto 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, 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 sprayed random powder (after grinding down to 1–3 μm) and by 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 the interpretation of the data. The content in organic matter, sulphides, hydroxyls and carbonates phases, was interpreted complimentary to CHNS, ICP-OES and XRD 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 atmospheras: N_2 and O_2 gas (20 mL/min). The external specific surface area was measured in 0.2–0.5 g of degased material (60 °C) by the Brunauer-Emmett-Teller (BET) method of nitrogen gas sorption at 77 K in Micromeritics Tristar II 3020 and Beckman Coulter SA-3100. The material was prepared from 1 g of original sample ground gently below 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®

(software version 3.62) assuming the refractive index and density of silica SiO_2 (1.457 and 2.65 g/cm^3). Samples were dispersed in distilled water by stirring at 2500 rpm speed and ultrasonic treatment. Measurements of 10 min duration were repeated in the same sample until the results were constant, to then take their average.

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 analyses. The solution was then centrifuged and filtered (0.45 μm) to measure the EC with a 4-mm sensor. 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 by TOC-V-CSH analyser (Shimadzu ASI-V). The cations in the exchange complex were determined as the difference between those extracted with a 1.26 M $SrCl_2$ solution (80 mL) minus the soluble ones 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 (HITACHI Polarized Zeeman Z2300), whereas ammonium was analysed by atomic emission spectroscopy. $LaCl_3$ was added at 20% to standards and samples for calcium and magnesium analyses. 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 a period of 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 (water content that separates the plastic and liquid states) and the plastic limit (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 20 mm into the wet sample, with duplicates differing ≤0.5 mm (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 3-mm diameter begin to crumble, with four replicates differing ≤2% moisture content of their plastic limit (BS 1377:2:5.3:1990 and ASTM D 4318,15). To know the range of water content in which the clayey material has a plastic consistency, the plasticity index was calculated as the difference between the liquid and the plastic limits (Head, 2006). All actual moisture contents were determined by mass % dry basis (Eq. 1) after oven drying 5–10 g of material (105 °C, 48 h) with duplicates that differ ≤0.5%

$$MC(\%) = \frac{m_w - m_d}{m_d} \times 100 \qquad (1)$$

where MC is the moisture content dry basis (%), m_w is the mass of wet sample before moisture removal (g), m_d is the mass of sample after drying (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 into a mould of 105-mm diameter and 115.5-mm high, in three layers subjected to 27 blows each one, by a 2.5 kg rammer of 50-mm diameter that drops from a height of 300 mm (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 triplicates at 20 °C, in desiccated materials of <2 mm size (50 g) using air-dried pycnometers of 50 mL (BS 1377:2:8.3:1990 but 20 instead of 25 °C). The porosity (V_{pore}) was therefore calculated following Eq. 2:

$$V_{pore}(\%) = \frac{V_{air} + V_{H2O}}{V_{tot}} \times 100 = \frac{V_{tot} - V_{solid}}{V_{tot}} \times 100 \quad \text{In the optimal condition: } V_{pore}(\%) = \frac{V_{tot} - \frac{m_{d,OMC}}{Gs}}{V_{tot}} \times 100 \quad (2)$$

where V_{air} is the volume of the air (mL), V_{H2O} is the volume of the water (mL), V_{tot} is the total volume (1000 mL, mould), V_{solid} is the volume of the solid particles (mL), and $m_{d,OMC}$ the dried mass of sample at the OMC (g).

Air void saturation lines (η_{air}) were drawn as a function of dry bulk density (γ_d) relative to the moisture content ratio (Eq. 3). The specific value for the air void saturation after compaction at the optimal conditions ($\eta_{air\ opt}$) was calculated with the γ_d and MC equal to MDD and OMC ratio, respectively (Eq. 4)

$$\gamma_d = \frac{(1 - \eta_{air}) \cdot G_s \cdot \gamma_{H2O}}{1 + MC \cdot G_s} \tag{3}$$

where γ_d is the dry bulk density (g/cm^3), η_{air} is the air void saturation in relation to the total volume (ratio), G_s is the specific gravity, γ_{H2O} is the density of water (1 g/cm^3) and MC is the moisture content ratio.

$$\eta_{air\ opt}(\%) = (1 - \frac{MDD\ (1 + OMC \cdot G_s)}{G_s \cdot \gamma_{H2O}}) \times 100 \tag{4}$$

3. RESULTS AND DISCUSSION

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 LC than in the rest. OC was notable for its high content in calcium, carbon, sulphur (g/kg) and strontium (mg/kg), with lower content in silica, iron and phosphorus. 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).
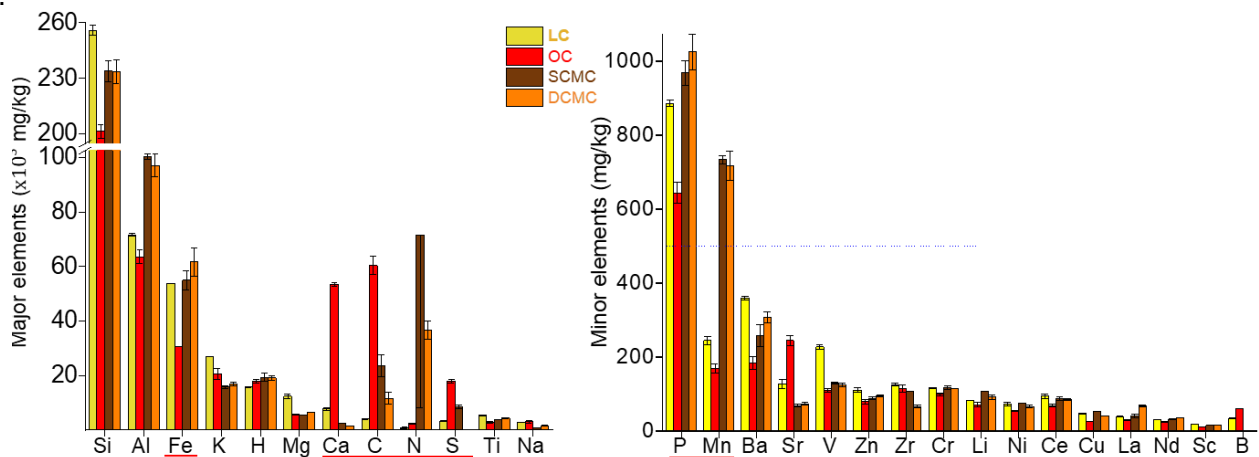

Figure 1. Elemental composition of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC).

The differences between the clayey substrata are due to their mineralogy and origin. 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 of illite/smectite (mixture of layers) in OC and the two Coal Measures Clays. Smectite is often found interstratified with illite and in mixtures with chlorite and sometimes kaolinite in deep sea marine sediments, as for LC and OC but not SCMC and DCMC which have a fluvio-deltaic origin. Another indication of the presence of smectite is the high silica-to-aluminium ratio, especially in LC (Weaver and Pollard, 1973).
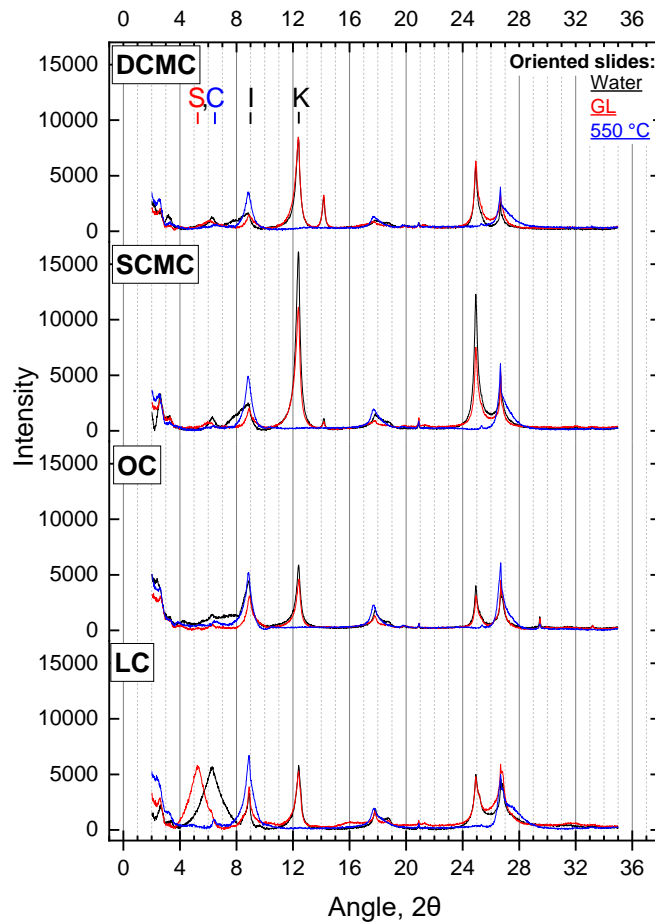
Figure 2. Sheet-silicate mineralogy of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). Water: water and air drying preparation, GL: glycerol and air drying preparation, 550 °C: water and 550 °C drying preparation. S: smectite d_{001} reflection under GL preparation, C (chlorite) and I (illite) d_{001} reflections under all three preparations. K: kaolinite d_{001} reflection under water and GL preparations.

Quartz and feldspars were the most important phases in all materials. These are accompanied by oxides except in 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 highest mass loss due to dehydroxylation (connected with the mass of clay minerals) was in Coal Measures Clays (5–9 %), while the highest mass loss due to organics, sulphides and carbonates phases corresponded to OC (3, 4 and 5% respectively). Particulate organic matter as an associated material in these clays was especially high in OC in the form of disseminated organic matter, coarse lignite fragments and vertebrate and invertebrate fossils. 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 (biodegradation).
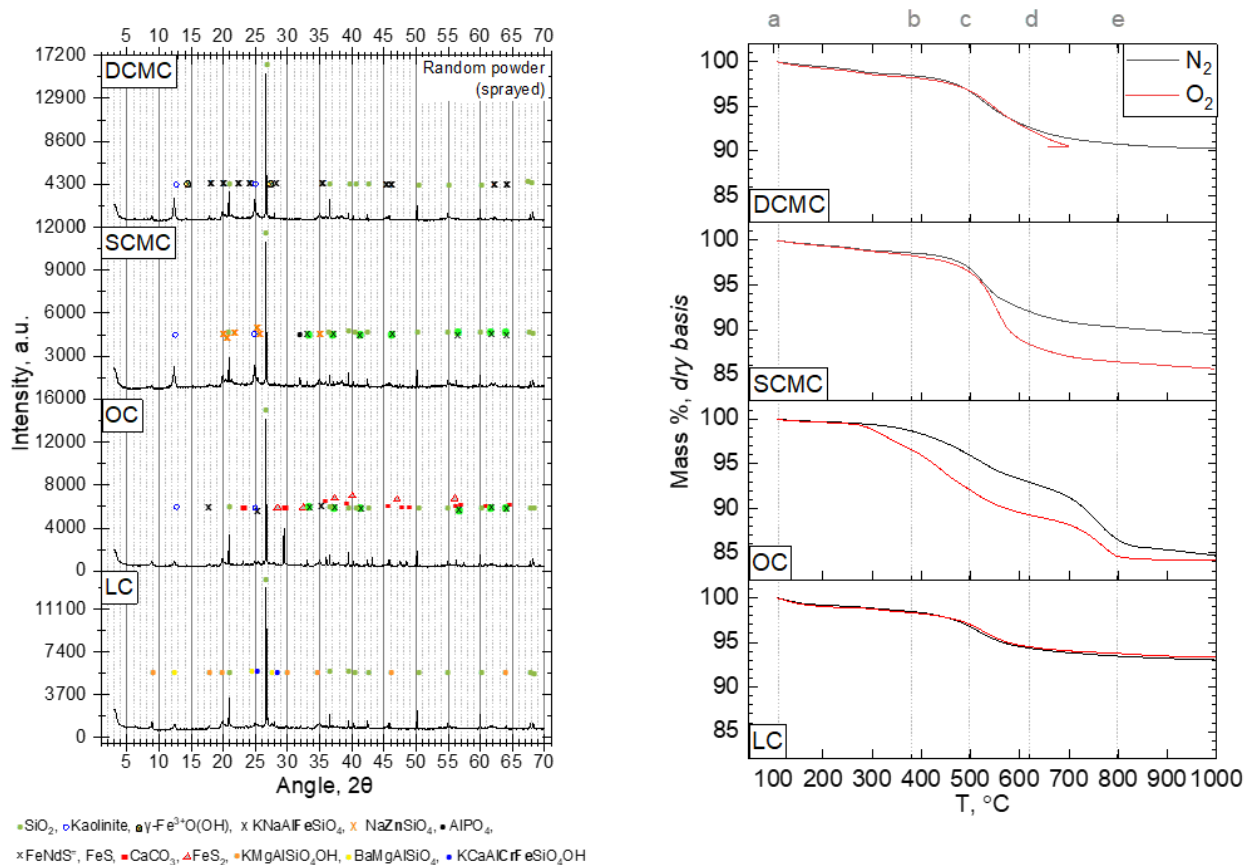
Figure 3. Left: Global mineralogy by sprayed random powder. Right: TGA curves with mass relative to the mass after dehydration: (a-b) Mass loss due to organic matter, (b-c) Mass loss due to sulphides, (c-d) Mass loss due to dehydroxylation, (d-e) Mass loss due to carbonate decomposition and (e-end) decomposition, recrystallisation.

3.2 Pore water and exchangeable cation compositions

The LC had the highest natural moisture content followed by OC (39 and 25 ± 2%, respectively), whereas SCMC and DCMC had the lowest values (10 and 12 ± 1%). This indicates a decreasing water absorption and porosity from LC > OC > Coal Measures Clays. The pore water composition of the clayey materials also showed some differences. OC was the most basic material due to the presence of calcium carbonate phases (pH 9.0) and LC was slightly basic with a pH of 7.3. In contrast, SCMC and DCMC were acidic with pH of 3.8 and 5.4, respectively (water/clay suspensions 2:1). The acidity in the latter case most likely arises from oxidation of pyrite in the upper, weathered zone, producing a low pH, gypsum and amorphous iron oxides as by-products. Acconcordingly, alkalinity was only present in OC (10.3 mmol/kg as $CaCO_3$) and LC (1.7 mmol/kg as $CaCO_3$). The absence of calcite in Coal Measures Clays explains their poor acid neutralization capacity. The total dissolved ion content, in terms of electrical conductivity, was between 1–3 mS/cm in the filtered pore water extracts (liquid to solid ratio 2:1), except for DCMC, which was only 0.1 mS/cm and for OC, which was 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 LC and OC, by magnesium (Mg^{2+}) and Ca^{2+} in SCMC and mostly Na^+ in DCM. In all cases the concentration of potassium (K^+) was very low and ammonium (NH_4^+) was not detected.

The surface of soil particles is critical for the chemical reactions, sorption, colloid filtration, and transport of contaminants. As expected, the exchangeable cations in the negatively charged sites of the clays and particulate organic matter were the same as those 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+}. The Ca^{2+} was released by dissolution of carbonate minerals in the extracting solution instead of replacement of the exchangeable cations. Thus, the CEC was measured directly instead of estimating this from the sum of exchangeable cations. The CEC at pH 7–8 decreased from LC (26 cmol+/kg) < OC (16 cmol+/kg) < Coal Measures Clays (13 cmol+/kg). All clayey materials and especially OC contained particulate organic matter (1 – 3 wt%) which also has a large surface area in addition to the CEC. Remarkably, the pore water of OC contained 10 mg/g of soluble carbon. The external specific surface area increased from LC < OC < DCMC < SCMC (9.281 ± 0.305, 12.759 ± 3.556, 31.030 ± 1.037, 53.735 ± 0.967 m^2/g). 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). However, the total surface area (external plus internal) of LC is expected to be the largest because of its content on expandable clay minerals.

3.3 Consistency and compaction properties

The moisture contents at plastic and liquid limits (PL and LL) were determined to identify clays susceptible to dispersion and excessive shrinkage in the field. These parameters are also useful to distinguish between silt- and clay- size, and organic or inorganic character. All clays have a LL >20%, confirming that they are cohesive materials (no sands). LL and PI decreased from LC > OC > Coal Measures Clays, consistent with the dominant sheet silicate in each material (smectite > illite(kaolinite) > kaolinite). LC and OC were fat (greasy) clays of 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 has plastic consistency (from 28 to 78%, i.e., PI = 50%), twice that of OC, the next in second place. This is due to the presence of smectite (expandable clay mineral) and the more clay-size particles expected in LC than in the other clays which have a higher silt content. The majority (90% by volume) of the particles in LC had a diameter < 62 µm, whereas in OC, SCM and DCM were 764, 675 and 253 µm as measured by laser diffraction. Smectites 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 two Coal Measures Clays gave similar results: lean clays of intermediate plasticity, medium toughness and high dry strength. The "A-line" on the plasticity chart (Figure 4) denotes the empirical boundary between inorganic materials and clays (above the line) and organic clays and clastic silts (below it). Both Coal Measures Clays and especially OC fell in the vicinity of organic silts, LC being noticeable for being a more inorganic clay. The dark grey colour of the former also reflects the higher particulate organic matter content.
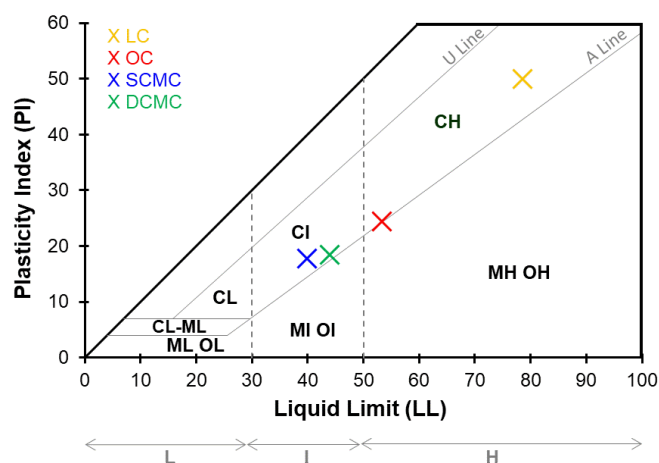

Figure 4. Soil classification and plasticity evaluation of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). L, I, H denote low, intermediate and high

plasticity. O denotes organic character. C denotes clayey and M denotes silty and/or sandy (Unified Soil Classification System, USCS). U-line is the upper bound of PI for natural soils defined by the two equations: $PI = 7$ if LLs ≤16, and $PI = 0.9\,(LL - 8)$ if LLs >16.

All materials had clays with intermediate to high plasticity, confirming the absence of dispersive clay fines. 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 rarely contain dispersive clays. In the case of LC, smectites are responsible for the adhesion forces between particles, which helps to prevent dispersion and thus soil erosion. Dispersive clays typically occur in soils classified as CL, sometimes also ML, CL-ML and CH lacking of smectite (Figure 4).

Clays are normally compacted for placing and constructing the clay liners because it increases the shear strength and bearing capacity, which limits future settlement. By compacting, the void ratio and permeability decrease, which consequently reduces the leakage of landfill leachate and seepage of groundwater flow. In addition, variations in volume change are less pronounced, and thus clays are less susceptible to cracking that would offer preferential flow paths for leachate mobilisation. To optimise this, clays should be compacted close to the OMC, which is the quantity of water necessary to achieve the maximum dry (bulk) density. Under the same compacted effort, the OMC decreased from LC > OC > Coal Measures Clays while the maximum dry (bulk) densities followed the inverse sequence (Figure 5). This sequence agrees with the one for air void saturation after compaction at the optimal conditions and the one for porosity, and with the higher plasticity of LC, followed by OC, which can accommodate more water to achieve their maximum dry densities than the Coal Measures Clays. Generally, soils dominated by clay-sized particles exhibit the highest OMCs whereas silt-rich soils have medium values and sandy materials have the lowest values. Accordingly, OC and LC exhibited the highest OMC (25-29% with maxima dry bulk densities of 1.44-1.46 g/cm^3, heavy clays) whereas the Coal Measures Clays the lowest (17% with maxima dry bulk densities of 1.78-1.80 g/cm^3, sandy-clay materials). The particle density of the solids, in terms of specific gravity, decreased from LC > Coal Measures Clays > OC due to the highest amount of particulate organic matter of the last one (Figure 5). Both Coal Measures Clays have very similar consistency and engineering behaviours (Figure 4 and Figure 5).
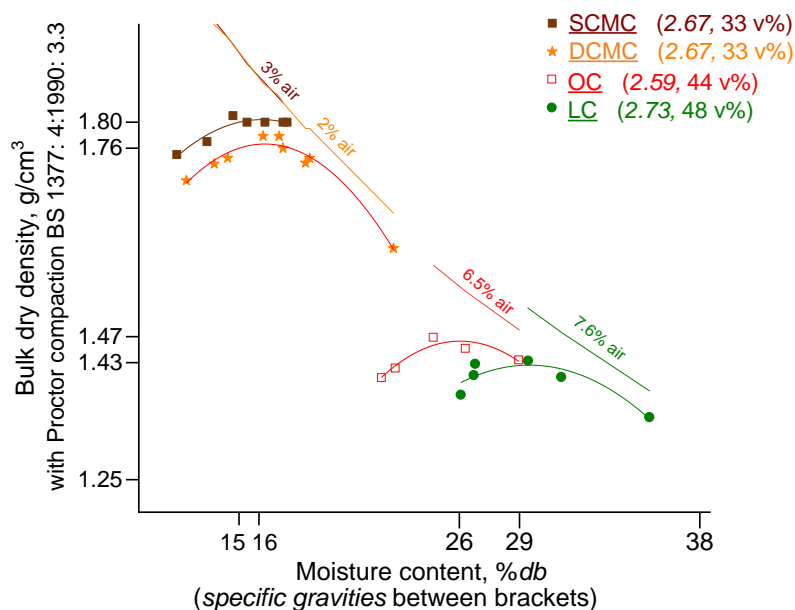

Figure 5. Comparison of compaction curves under Proctor BS 1377:4:3.3:1990 to estimate the (optimum) moisture content at which the maximum dry bulk densities occur. Air void saturation lines (v% of the total volume) at the optimal conditions. LC: London clay, OC: Oxford clay, SCMC: shallow Coal Measures Clay and DCMC: deep Coal Measures Clay (specific gravities and porosities between brakets).

3.4 Evaluation as landfill liners

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 sodium, potassium, bicarbonate and chloride, with significant ammonium and organic compounds. The heavy metal content is generally relatively low, often at not major concern and limited to chromium, nickel and zinc (Aucott 2006; Kjeldsen et al., 2002). In addition to the low permeability that they provide, compacted clays can attenuate these leachate pollutants by sorption, dilution, redox transformations, biodegradation, precipitation and filtration (Allen, 2001; Griffin et al., 1976). 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 leachate pollutant. By sorption, pollutants are attached to mineral phases or particulate organic matter by a physical or chemical process and encompasses ion exchange, adsorption, absorption and chemisorption. By redox transformations, organic and metal compounds are converted 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.

For sorption, the CEC is very important in clay minerals and particulate organic matter. In this case, cations are sorbed from the pore water by clays to neutralize the negative charge created by unbalanced substitutions of their structural cations. Naturally sorbed cations can be replaced by cationic pollutants in the leachate. In the case of ammonium and potassium from leachate, illites (OC, Coal Measures Clays and LC) have high affinity for selective sorption of these species due to their size compatibility with the interlayer (exchange) sites in the clay lattice (Griffin et al., 1976). Smectites (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 or organic cations or organometallic complexes in leachate, smectites sorbed these species preferentially relative to smaller, inorganic or uncomplexed metals. 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 provide an exchanger interlayer space large enough to accommodate them. CEC varies with pH, generally increasing with pH due to the development of greater negative charge (average pH in leachate is 7–8). Smectite, along with vermiculite (interlayer Mg), provide high CEC, while illites provide mid-range values and kaolinite very low values. Thus the capacity to reduce the concentration of cationic pollutants in leachate by cation exchange reactions decreases from LC > OC > Coal Measures Clays. 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 (LC and Coal Measures Clays) associated with clays (Raymahashay, 1987). Bicarbonate is the major compound of leachate and largely determine the acid-base neutralisation potential of the system. This is important where carbonate minerals are scarce (Coal Measures Clays) to attenuate acidic episodes such as oxidation of sulphides (pyrite) by infiltrating rainwater or acetogenic leachate (from fresh waste). Chloride can be attenuated to a lesser extent by retention in apatite crystals and in clay minerals (Koutsopoulou and Kornaros, 2010), but mainly diffuses through the clay liner, together with sodium 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). These elements are diluted by the receiving groundwater and are generally not a problem due to its non-toxicity even at high concentrations. Sulphate in leachate is attenuated by anaerobic microbial reduction, a common redox process in landfills (Batchelder et al., 1998), supporting metal sulphide precipitation in the liner and low concentrations of sulphate 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

or sulphate-reducing), one or other organic compounds are biodegraded. The concentration of the oxidising agents and their reduced species in the leachate indicates the redox conditions (Taylor and Allen, 2006). All the studied clayey substrata content redox-sensitive species, the most important being pyrite in OC and SCMC and iron oxides in LC, SCMC, DCMC. Differences in clay minerals have a minor effect on the biodegradation of organic pollutants than on the (already discussed) sorption of inorganic pollutants. This is because organic pollutants are attenuated mainly by anaerobic biodegradation rather than by sorption to clay minerals (Adar and Bilgili, 2015). Their decomposition to ultimately 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 presence found in 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 through 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. OC and SCMC contain pyrite, and LC, SCMC, DCMC contain iron/metal oxides. The high native particulate organic matter content of OC favours the sorption of metals, whereas the dissolved organic compounds of leachate favours the formation of 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).

Regarding hydraulic conductivity, the four clayey substrata all meet the relevant design criteria and are candidates for use in a landfill liner. Materials with at least 20% LL, 7% PI, 30% fines and 15% clays have hydraulic conductivities below 10^{-9} m/s, the maximum regulatory criterion in the EU and most countries (Benson et al., 1994). Coal measures Clays were the easiest to compact until negligible air is present in their voids, which is convenient for low leachate permeability of the liner.

LC is the only one that contains significant amounts of smectites among its clay minerals. These are expandable sheet silicates with desirable properties such as erosion resistance, low permeability and the best ability to attenuate pollutants. Thus, they have been used globally to improve landfill liners (Ruiz et al., 2012). A key limitation is that smectites have high plasticity and may shrink most when in contact with leachates. This 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). A further drawback of smectites is their alteration to newly formed illite or even kaolinite, resulting in much less chemo-mechanical stable materials than originally kaolinite-rich and illite-rich samples not derived from smectite (Zhao et al., 2007). This illitization at the expense of the smectite content would occur after ammonium and potassium sorption from the landfill leachate (Regadío et al., 2015). Its consequent impact on the clay CEC due to the decrease of the smectite component would be a minor impact, since in these cases CEC normally decreases by ≤10%.

4. 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. All materials can achieve a low hydraulic conductivity to meet relevant liner design specifications and minimise leachate migration. 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. These compounds 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 after sorption of pollutants can be diluted by rainfall and groundwater without harmful effects.

All studied clayey materials are useful for the attenuation of leachate pollutants in sustainable waste landfills. However, different management options should be applied depending on the clayey material. LC is the best material based on the sorption capacity and erosion resistance. However, 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. OC is also plastic but to a lesser extent, with an acceptable plastic index. This substratum has a significant sorption capacity and is the best material for buffering acid leachates (native calcite) and degrading organic compounds. On the negative side, Coal Measures Clays have the lowest sorption capacity and null 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 the easiest to compact until no or negligible air voids, which favours low hydraulic conductivities. SCMC contained sulphate-bearing species (resulting from oxidation of pyrite) that enhance the retention of heavy metals. DCMC had very low mineral phases or inorganic salts that are readily dissolved in water, which is advantageous because of less mobilization of leachable salts from the liner itself. LC and Coal Measures Clays have associated iron/metal oxides and oxyhydroxides that can enhance anion exchange and the removal of metals by sorption. The redox-sensitive species pyrite (OC and SCMC) and iron oxides (LC and Coal Measures Clays) can enhance the removal of metals by redox transformation and precipitation. This presence of pyrite and iron oxides also determine to a large extent the acid-base neutralisation potential, together with native carbonates in OC and bicarbonates in the leachate.

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