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Carbonation in stabilised peat: an accelerated pilot study

Carbonation dans la tourbe stabilisée: une étude pilote accélérée

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ABSTRACT Due to stringent environmental regulations, embodied carbon estimates are being used increasingly to assess the environmental impact of major building and infrastructure projects, including their geotechnical components. The focus of this paper is on the ground improvement technique of soil-mixing. While it is established that improper management of excavated peat can cause it to lose the majority of its carbon to the atmosphere as CO₂, the carbon response of peat mixed *in situ* is unknown and has prompted this study. Under accelerating conditions in the laboratory, emissions were recorded from columns of parent peat (high and low water tables) and cement-stabilised peat. While the parent peat was found to be a source of CO₂ influenced by water levels and temperature, stabilised peat appears to act as a net carbon sink. This is an important finding for carbon calculations relevant to soil-mixing applications.

RÉSUMÉ En raison de réglementations environnementales strictes, les estimations de carbone contenu sont utilisées de plus en plus pour évaluer l'impact environnemental des grands projets de construction et d'infrastructure, y compris leurs composants géotechniques. L'objectif de cet article est la technique d'amélioration de sol du sol-mélange. Bien qu'il soit établi que la mauvaise gestion de la tourbe excavée peut lui faire perdre la majorité de son carbone dans l'atmosphère sous forme de CO₂, la réponse carbone de la tourbe mélangée *in situ* est inconnue et a incité cette étude. Sous des conditions d'accélération dans le laboratoire, les émissions ont été enregistrées dans les colonnes de tourbe mère (nappe phréatique élevée et basse) et de tourbe stabilisée par le ciment. Bien que la tourbe mère se soit révélée être une source de CO₂ influencée par le niveau d'eau et la température, la tourbe stabilisée semble agir comme un puits net de carbone. Il s'agit d'une découverte importante pour les calculs de carbone pertinents pour les applications du sol-mélange.

1 INTRODUCTION

Construction on peatlands normally requires some form of ground improvement, with techniques such as excavate-and-replace, piling and dry soil-mixing generally considered the best options. Dry soil-mixing is a ground improvement technique that requires the injection of a dry binder, with cement or a combination of cement and ground granulated blast furnace slag (GGBS) typically providing the greatest strength gain in peat (Timoney et al. 2012).

Increasingly, construction options for a project, such as the ground improvement techniques mentioned, are appraised based upon detailed embodied carbon (EC) calculations as well as the traditional considerations of cost and programme (Inui et al.

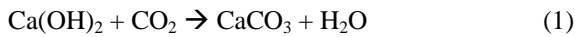
2011). EC is associated with greenhouse gas emissions (GHGs) released over the lifetime of a product. It accounts for the global warming potential of various GHGs and is measured in carbon dioxide equivalents (CO₂eq), which includes carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and perfluorocarbons (PFCs) (Hill et al. 2011). EC calculations are increasingly sought to demonstrate compliance with environmental regulations.

In projects involving an excavate-and-replace solution, peat is often removed to disposal areas and the subsequent drying causes a significant release of CO₂ into the atmosphere (Nayak et al. 2008). While it is acknowledged that the binder used in soil-mixing applications can be environmentally costly in terms of carbon emissions, the fact that the peat remains in-

situ may be an advantage despite the considerable reduction in moisture content (often hundreds of percent) that occurs upon stabilisation. However, the impact of stabilising peat on overall CO₂ emissions has not been considered to date. Duggan et al. (2015) assumed no net carbon output from stabilised peat in an EC appraisal of geotechnical options for an Irish motorway scheme, but pre-empted the need for research in this area. In this paper, results of a pilot laboratory study are reported in which the emissions for a raw Irish peat (with both high and low water tables modelled) and stabilised peat are compared and the implications for soil-mixing are assessed.

2 CARBONATION IN CONCRETE

The calcination of limestone represents approximately half the CO₂ emissions from cement production, with cement consuming about the same amount in its lifetime in a process called carbonation (Engelson et al., 2005). Carbonation is a well-established phenomenon in concrete. CO₂ from the atmosphere must first dissolve in water, forming carbonate ions, before the dissolved CO₂ reacts with calcium hydroxide (Ca(OH)₂) from the cement paste, forming the calcium carbonate (CaCO₃) precipitate (Eqn. 1).



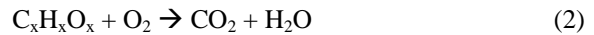
CO₂ must diffuse through a carbonated surface to reach uncarbonated concrete. As Ca(OH)₂ is consumed, the pH will drop, resulting in all Ca compounds such as calcium silicate hydrate dissolving over time and forming CaCO₃ along with other carbonates such as silica gels, metal hydroxides and clays (Lagarblad, 2005). Since Ca(OH)₂ has a pH of 12.5 and CaCO₃ has a pH of 9.4, carbonation reduces the pH of the concrete, destroying the passivity (protective oxide layer) of the embedded steel reinforcement bars, making it susceptible to corrosion (Papadakis & Vayenas 1991).

The factors most likely to affect the carbonation speed include degree of hydration, relative humidity, moisture content, temperature, concrete quality, particle size, external environment, porosity and the partial pressure of CO₂ (Engelson et al. 2005).

3 CARBONATION IN STABILISED PEAT

Based upon analogies with concrete carbonation and the reality that CO₂ and water are present in almost every environment, stabilised peat should also be susceptible to carbonation. A carbonation process in stabilised peat is postulated in this section. Carbonation in peat is likely to involve a more complex gas diffusion process than in concrete, involving diffusion from a carbonated surface to freshly stabilised peat, not only by atmospheric CO₂ but also CO₂ released by peat oxidation, as described below.

Dead plant and animal decomposition occurs rapidly in the aerobic layer (above the water table) where organic compounds (C_xH_xO_x) are oxidised, releasing CO₂ (Lindsay 2010) (Eqn. 2). Decay also occurs at a lesser rate in the anaerobic layer (under the water table) where CH₄ is produced. CH₄ may then diffuse into the aerobic layer where it comes in contact with oxygen (O₂), producing further CO₂ and water (Couwenberg 2009) (Eqn. 3).



Carbonation may occur in the aqueous phase, either at the stabilised peat surface which is exposed to precipitation or anywhere in the stabilised mass where groundwater is present. Most of the carbonation rate factors cited in Section 2 will also be relevant to peat; however, instead of concrete quality, the amount/type of binder and the gas diffusion coefficient of peat will be influential. A postulated relationship between amount of carbonation and depth is shown in Figure 1, identifying a carbonation front.

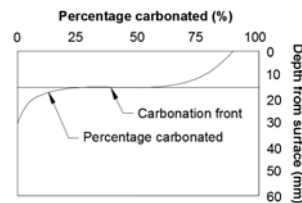


Figure 1. Postulated relationship between percentage carbonated and depth in stabilised peat

The carbonation rate will decelerate with time as the carbonation front, through which O₂ and CO₂ must pass, deepens with time. Given that Houst

(1996) demonstrated that the diffusivity of CO₂ in cement is always lower than that of O₂, mainly due to the difference in size of the two molecules, the release of CO₂ due to peat oxidation may occur before atmospheric CO₂ diffuses to the same level.

Furthermore, stabilised peat submerged in water will carbonate more slowly as diffusion in a liquid is about 10⁴ times slower than in air (Houst 1996). Consequently, the availability of CO₂ released from the peat will be limited as the capillary system will be blocked with water, and CO₂ and O₂ will have difficulty diffusing into the cement.

The decelerating carbonation rate is also related to a volume increase associated with the transformation of Ca(OH)₂ to crystallographic forms such as calcite (CaCO₃) in Eqn. 1; for example, the formation of calcite engenders a volume change of 12% (Houst 1996). This in turn fills empty pore space, densifying and strengthening the stabilised peat. The cement paste over time will revert to its basic components in cement production (e.g. to rock types such as limestone). Therefore, it can be concluded that stabilised peat will carbonate; and while the duration of the process is unknown, it may be within the structure/infrastructure's lifecycle that it supports.

4 METHODOLOGY

4.1 Initial experimental conditions

The peat used in this study was retrieved from a cut-over upland blanket bog at a windfarm site in Co. Mayo, Ireland. It was classified as H2-H4 on the Von Post scale with a pH ranging from 5.0 to 5.15 (sample size, n=6). The following test results were determined (with the ± referring to one standard deviation from the mean): bulk density of 955 ± 23 kg/m³ (n=5), organic content of 88 ± 13% (n=9), and moisture content 949 ± 221% (n=9).

The 228-day study involved the assembly of nine hollow acrylic cylindrical columns (10 cm in diameter × 65 cm in height containing 50 cm of peat) as shown in Figure 2(a); standpipes were connected to the bottom of each one and sealed outside with silicone. The columns were kept in a temperature-controlled room (Figure 2(b)), with an initial temperature of 15°C and a relative humidity of 60-90%. The columns were left in darkness, except while gas sam-

pling, and thereby allowing little plant growth. In the room, the CO₂ concentration was kept high, ranging from 500 ppm to 1500 ppm, with an average of 800 ppm to represent underground CO₂ concentration conditions, which are higher than in the atmosphere. The high temperatures and CO₂ levels, in addition to the absence of a surcharge in the case of stabilised columns (leaving the structure more porous), were imposed deliberately with a view to accelerating the carbonation process.

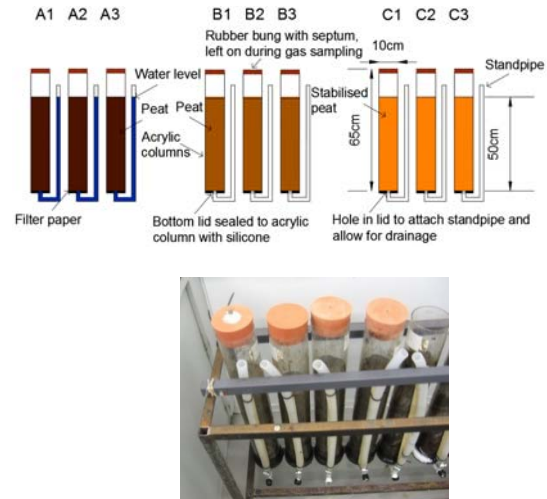


Figure 2. (a) Schematic of experiment (above) and (b) Photograph of columns during gas sampling (below)

As illustrated in Figure 2(a), three of the columns contained raw peat with the water table at the surface (A1-A3) and three contained raw peat with the water table at the bottom (B1-B3). To keep the water table at the surface in A1-A3, the samples were topped up with rainwater daily. The peat in B3 was mixed to simulate the mass stabilisation of peat, but binder was not added. The final three columns contained stabilised peat (C1-C3) with the water table at the bottom; 250 kg/m³ of cement (CEM II A/L 32.5N) binder was mixed with peat in a mixer and subsequently placed into the columns. The moisture content of the stabilised material was measured immediately after mixing and was found to have decreased from 986 ± 199% (n=3) to 237 ± 28% (n=3). After 228 days these moisture contents had reduced marginally, possibly due to further cementitious reactions and evaporation.

4.2 Subsequent modifications

On day 90, samples A1-A3 were drained, while the water table in B1-B3 was restored to the peat surface to simulate a peatland restoration scenario. This ‘reversal’ was intended as an additional check on the effect of water level on emissions assessed over the first 90 days. It was suspected that columns C1-C3 would become a CO₂ source due to the lack of water available (due to evaporation) for carbonation to occur. Consequently, after day 90, it was decided that these columns would receive 20 ml/day of rainwater, equivalent to 2.94 mm/day in keeping with the average annual rainfall in the west of Ireland of 2.7-3.4 mm/day (Met Éireann 2014). The room temperature was changed three times to investigate the impact of temperature: on day 137, from 15°C to 20°C; on day 194, from 20°C to 10°C; and on day 227 from 10°C to 20°C. All events are summarised in Table 1.

Table 1. Experimental conditions summary table

Time (days)	Temp. (°C)	Water Conditions		
		A1-A3 (Peat)	B1-B3 (Peat, B3 mixed)	C1-C3 (stabilised)
1-90	15	Waterlogged	Drained	Drained
90-137	15	Drained	Waterlogged	Water added
137-194	20	Drained	Waterlogged	Water added
194-227	10	Drained	Waterlogged	Water added
227-228	20	Drained	Waterlogged	Water added

4.3 Gas sampling

Gas emissions were initially taken every 1 to 3 days, but later to maximum intervals of 29 days. When a change in a variable such as water level or temperature occurred, a gas emission reading was taken shortly before and after. Before gas sampling, air was circulated over each column and a rubber bung placed on each column for one hour. Samples were retrieved from the void above the peat at 0, 20, 40, and 60 minutes, inserted into 3.7 ml pre-evacuated vials and their constituents examined for CO₂ and CH₄ concentrations using an Agilent 7890A GC (Agilent Technologies Ireland Ltd., Cork, Ireland). For each sampling event, the flux rate was calculated by collecting four gas samples and determining the change in gas concentration over time.

5 RESULTS

5.1 Peat columns A1-A3

The average combined CO₂ and CH₄ emission levels for each column category (along with their standard deviation on each day of measurement) are presented as a flux rate in Figure 3. Specimens A1-A3 initially experienced high short-term levels of CH₄ release, particularly significant given that CH₄ has a Global Warming Potential (GWP) of 25, whereas CO₂ has a GWP of 1. Emission levels then stabilised, reducing from 477 ± 496 mgCO₂eq/m²/hr (± 1 standard deviation) over the first four days to 49 ± 33 mgCO₂eq/m²/hr from day 6 to day 89 (Figure 3(a)).

On day 90 after water levels were lowered, short-term high levels of CH₄ gas were noted again. This is consistent with observations made in wetlands where major fluxes of CH₄ arose after a drop in the water table due to drought (Couwenberg 2009). Gas emissions then decreased to drained peat emission levels, i.e. compatible with levels in B1-B2 before day 90.

Thereafter, in Specimens A1-A3, emissions fluctuated according to temperature, first increasing to an average of 223 ± 61 mgCO₂eq/m²/hr at 20°C, then decreasing to 68 ± 46 mgCO₂eq/m²/hr at 10°C and finally increasing on day 228 at 20°C.

5.2 Peat columns B1-B3

Specimens B1-B2 also experienced high levels of CO₂ emissions in the first four days but decreased to 224 ± 28 mgCO₂eq/m²/hr from day 6 to day 89 (Figure 3(b)). Specimen B3 behaved differently in that it was a small source at first; however, between days 16 and 89 it acted similarly to Specimens B1-B2 (Figure 3(c)). On day 90, water levels were restored in B1-B3 and emissions immediately decreased to levels compatible with A1-A3 up to day 90.

In Specimens B1-B3, following the change of temperature on day 137, emissions increased dramatically. Notably in B3, overall emissions increased 82 fold due to very high concentrations of CH₄ (Figure 3c); evidently, the disturbed peat was more sensitive to temperature change than A1-A3 and B1-B2. Even when the temperature was decreased from 20°C to 10°C on day 194, emissions remained relatively high, suggesting that time might have been required for the microbes in the peat to readjust. It is likely that mix-

ing the peat caused organic components to be broken down into more readily biodegradable material by generating a larger surface area for methanogens to digest. This resulted in high levels of anaerobic decomposition occurring when water levels were changed and temperatures increased, leading to high CH₄ and CO₂ production (Couwenberg 2009).

5.3 Stabilised peat columns C1-C3

In contrast to tests A1-A3 and B1-B3, the stabilised peat (C1-C3) initially acted as a carbon sink, with average rates recorded in the first 4 days of -196 ± 69 mgCO₂eq/m²/hr. However, in keeping with the argument in Section 3, as expected, the carbonation rate gradually decreased to a steady carbon intake of -55 ± 41 mgCO₂eq/m²/hr between day 6 and day 89 (Figure 3(a)). Even though rainwater was added on and after day 90, two of these columns were, in fact, a small CO₂ source on day 116, the highest being C2 at 17 mgCO₂eq/m²/hr. Specimens C1-C3 also reacted to the temperature increase, with a higher carbonation rate averaging -38 ± 24 mgCO₂eq/m²/hr after day 137, but this then decreased slightly to -35 ± 21 mgCO₂eq/m²/hr from day 194 onwards. CH₄ was not detected in emissions from the stabilised peat.

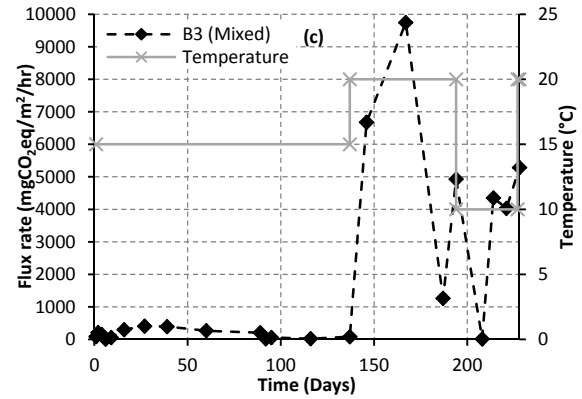
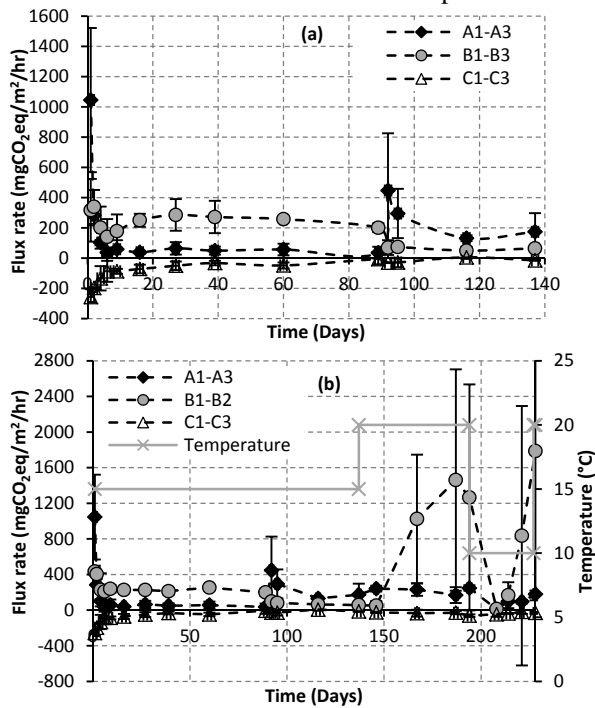


Figure 3. (a) Flux rates for Day 1-137 for A1-A3, B1-B3 and C1-C3 (top) (b) Flux rates for Day 1-228 for A1-A3, B1-B2 and C1-C3 (middle) (c) Flux rate for Day 1-228 for B3 (Mixed) (bottom)

5.4 Carbonation potential

Since the rate at which CO₂ is released from raw peat (due to oxidation) and absorbed by stabilised peat can be interpreted from Figure 3, it is possible to calculate how much carbonation (CO₂ Carbonation) has occurred using the CO₂ balance in Eqn. 4. By excluding CO₂ taken in from the air, the carbonation rate will be underestimated slightly; however, as the majority of the CO₂ will be absorbed from oxidised peat as witnessed in this study, it is deemed acceptable.

$$\text{CO}_2 \text{ Carbonation} = \text{CO}_2 \text{ intake from stabilised peat} - \text{CO}_2 \text{ emissions from peat} - \text{CO}_2 \text{ intake from air} \quad (4)$$

As discussed for concrete in Section 2, the carbonation potential (C_p) of the three stabilised peat columns was approximately half the EC of cement as shown in Eqn. 5. (Clear et al. 2009, Engelson et al. 2005). Using $\text{EC} = 0.815 \text{ kgCO}_2/\text{kg}$ for cement and a mass of cement (M) used in these experiments ranging between 0.72 kg to 0.82 kg, C_p was found to range from 0.29 kgCO₂ to 0.33 kgCO₂ per column.

$$C_p = 0.5 \times M \times \text{EC} \quad (5)$$

The percentage of carbonation can be estimated as $\text{CO}_2 \text{ Carbonation}/C_p$. For instance, adopting $\text{CO}_2 \text{ emissions from peat} = 244 \text{ mgCO}_2\text{eq}/\text{m}^2/\text{hr}$ (21.4 tCO₂eq/ha/yr) as the average emission rate for B1-B3 from day 1 to day 89), it can be deduced that 3.0% to 3.6% of the carbonation potential had materialised.

It was also possible to estimate the time for full carbonation to occur. Flux rates were initially converted from $\text{mgCO}_2\text{eq/m}^2/\text{hr}$ to $\text{tCO}_2\text{eq/ha/yr}$. Then, using both lower and upper quartile flux intake rates from stabilised peat of $-6 \text{ tCO}_2\text{eq/ha/yr}$ ($-68 \text{ mgCO}_2\text{eq/m}^2/\text{hr}$) and $-2 \text{ tCO}_2\text{eq/ha/yr}$ ($-23 \text{ mgCO}_2\text{eq/m}^2/\text{hr}$) together with peat emission rates of $11 \text{ tCO}_2\text{eq/ha/yr}$ and $23 \text{ tCO}_2\text{eq/ha/yr}$, the time required for full carbonation was calculated to fall between 15 and 38 years. This is important when performing a life cycle assessment (LCA) on infrastructure built on stabilised peat, as emissions from stabilised peat may occur after carbonation is completed.

CONCLUSIONS

A pilot study examining CO_2 emissions from raw and stabilised peat specimens was conducted in the laboratory using accelerating factors. The following conclusions were drawn:

- Results from the peat columns A1-A3 indicated that when constructing on peatlands, peat disturbance should be kept to a minimum. Short-term high concentrations of CH_4 are emitted when peat is excavated or when water table levels are quickly changed.
- As dramatically observed in B1-B3, CH_4 production in peatlands strongly depends on water level and temperature, which also demonstrates the dramatic impact climate change may have on peatlands, progressively changing them from carbon sinks to carbon sources.
- Stabilised peat appeared to not only hold its carbon in C1-C3, but the binder used seemed to uptake CO_2 both from the atmosphere and the peat.
- Although emissions from mixed peat (B3) are high at 20°C , the net flux from the stabilised columns was a net intake due to carbonation.

It can be concluded from the results that soil-mixing, in terms of EC calculations and environmental impact, may be more environmentally acceptable than previously thought. Laboratory studies are ongoing to investigate the carbonation potential in stabilised peat which will allow engineers to calculate

more accurately the embodied carbon and environmental impact of dry soil-mixing in peatlands.

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