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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 CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub>, 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 CO<sub>2</sub> 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.

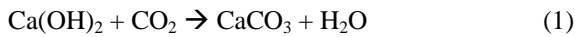
2011). EC is associated with greenhouse gas emissions (GHGs) released over the lifetime of a product. It accounts for the global warming potential of various GHGs and is measured in carbon dioxide equivalents (CO<sub>2</sub>eq), which includes carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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. CO<sub>2</sub> from the atmosphere must first dissolve in water, forming carbonate ions, before the dissolved CO<sub>2</sub> reacts with calcium hydroxide (Ca(OH)<sub>2</sub>) from the cement paste, forming the calcium carbonate (CaCO<sub>3</sub>) precipitate (Eqn. 1).



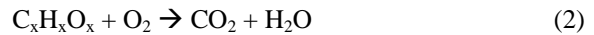
CO<sub>2</sub> must diffuse through a carbonated surface to reach uncarbonated concrete. As Ca(OH)<sub>2</sub> is consumed, the pH will drop, resulting in all Ca compounds such as calcium silicate hydrate dissolving over time and forming CaCO<sub>3</sub> along with other carbonates such as silica gels, metal hydroxides and clays (Lagarblad, 2005). Since Ca(OH)<sub>2</sub> has a pH of 12.5 and CaCO<sub>3</sub> 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 CO<sub>2</sub> (Engelson et al. 2005).

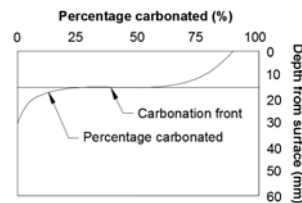
## 3 CARBONATION IN STABILISED PEAT

Based upon analogies with concrete carbonation and the reality that CO<sub>2</sub> 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 CO<sub>2</sub> but also CO<sub>2</sub> 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<sub>x</sub>H<sub>x</sub>O<sub>x</sub>) are oxidised, releasing CO<sub>2</sub> (Lindsay 2010) (Eqn. 2). Decay also occurs at a lesser rate in the anaerobic layer (under the water table) where CH<sub>4</sub> is produced. CH<sub>4</sub> may then diffuse into the aerobic layer where it comes in contact with oxygen (O<sub>2</sub>), producing further CO<sub>2</sub> 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 O<sub>2</sub> and CO<sub>2</sub> must pass, deepens with time. Given that Houst

(1996) demonstrated that the diffusivity of CO<sub>2</sub> in cement is always lower than that of O<sub>2</sub>, mainly due to the difference in size of the two molecules, the release of CO<sub>2</sub> due to peat oxidation may occur before atmospheric CO<sub>2</sub> diffuses to the same level.

Furthermore, stabilised peat submerged in water will carbonate more slowly as diffusion in a liquid is about 10<sup>4</sup> times slower than in air (Houst 1996). Consequently, the availability of CO<sub>2</sub> released from the peat will be limited as the capillary system will be blocked with water, and CO<sub>2</sub> and O<sub>2</sub> 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)<sub>2</sub> to crystallographic forms such as calcite (CaCO<sub>3</sub>) 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.

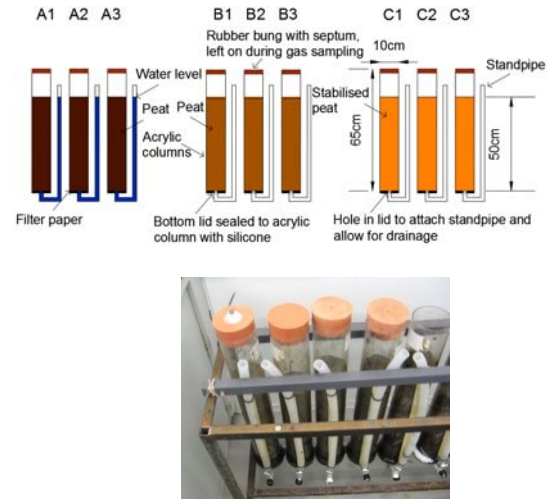
## 4 METHODOLOGY

### 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/m<sup>3</sup> (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 CO<sub>2</sub> concentration was kept high, ranging from 500 ppm to 1500 ppm, with an average of 800 ppm to represent underground CO<sub>2</sub> concentration conditions, which are higher than in the atmosphere. The high temperatures and CO<sub>2</sub> 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/m<sup>3</sup> 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 CO<sub>2</sub> 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 CO<sub>2</sub> and CH<sub>4</sub> 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 CO<sub>2</sub> and CH<sub>4</sub> 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 CH<sub>4</sub> release, particularly significant given that CH<sub>4</sub> has a Global Warming Potential (GWP) of 25, whereas CO<sub>2</sub> has a GWP of 1. Emission levels then stabilised, reducing from  $477 \pm 496$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr ( $\pm 1$  standard deviation) over the first four days to  $49 \pm 33$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr from day 6 to day 89 (Figure 3(a)).

On day 90 after water levels were lowered, short-term high levels of CH<sub>4</sub> gas were noted again. This is consistent with observations made in wetlands where major fluxes of CH<sub>4</sub> 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  $223 \pm 61$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr at 20°C, then decreasing to  $68 \pm 46$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr at 10°C and finally increasing on day 228 at 20°C.

### 5.2 Peat columns B1-B3

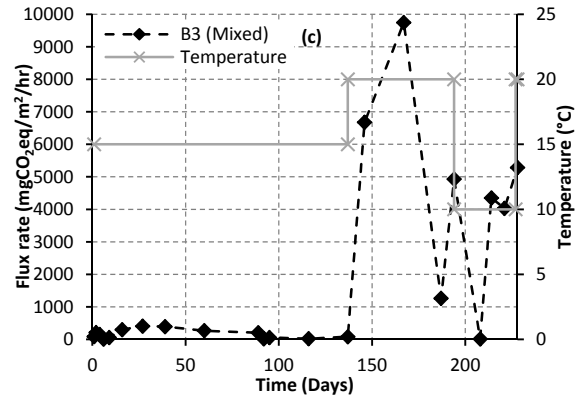
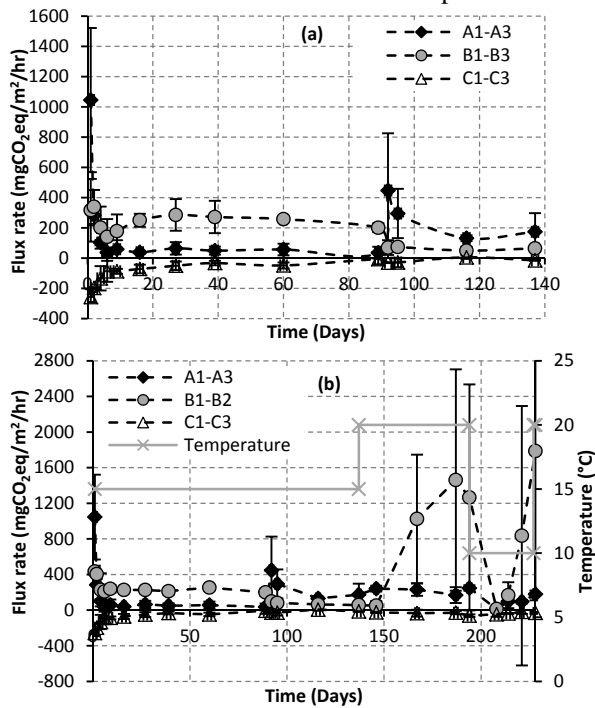
Specimens B1-B2 also experienced high levels of CO<sub>2</sub> emissions in the first four days but decreased to  $224 \pm 28$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr from day 6 to day 89 (Figure 3(b)). Specimen B3 behaved differently in that it was a small source at first; however, between days 16 and 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 CH<sub>4</sub> (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 CH<sub>4</sub> and CO<sub>2</sub> 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  $-196 \pm 69$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr. However, in keeping with the argument in Section 3, as expected, the carbonation rate gradually decreased to a steady carbon intake of  $-55 \pm 41$  mgCO<sub>2</sub>eq/m<sup>2</sup>/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 CO<sub>2</sub> source on day 116, the highest being C2 at 17 mgCO<sub>2</sub>eq/m<sup>2</sup>/hr. Specimens C1-C3 also reacted to the temperature increase, with a higher carbonation rate averaging  $-38 \pm 24$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr after day 137, but this then decreased slightly to  $-35 \pm 21$  mgCO<sub>2</sub>eq/m<sup>2</sup>/hr from day 194 onwards. CH<sub>4</sub> 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 CO<sub>2</sub> 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 (CO<sub>2</sub> Carbonation) has occurred using the CO<sub>2</sub> balance in Eqn. 4. By excluding CO<sub>2</sub> taken in from the air, the carbonation rate will be underestimated slightly; however, as the majority of the CO<sub>2</sub> 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 kgCO<sub>2</sub> to 0.33 kgCO<sub>2</sub> 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 CO<sub>2</sub> emissions from peat = 244 mgCO<sub>2</sub>eq/m<sup>2</sup>/hr (21.4 tCO<sub>2</sub>eq/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  $\text{CO}_2$  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  $\text{CH}_4$  are emitted when peat is excavated or when water table levels are quickly changed.
- As dramatically observed in B1-B3,  $\text{CH}_4$  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  $\text{CO}_2$  both from the atmosphere and the peat.
- Although emissions from mixed peat (B3) are high at  $20^\circ\text{C}$ , 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.

## ACKNOWLEDGEMENT

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