Chapter 5
Mathematical Modelling and Simulation of Chemical and Biological Reaction in Peat Solidification Work for Environmental Sustainability

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Abstract Understanding the chemical and biological mechanisms of peat solidification is vital to protect the environment during geotechnical works. The alteration of peat to increase its strength for the preparation of road construction requires an admixture to be added to the soil. Changes in peat properties affect proximal ecosystems. Peat has a high water content of up to 2000%, is high in fibre and microorganisms and has a low shear strength of around 4–12 kPa. Normal construction work requires around 300 kPa of soil bearing capacity. The addition of admixtures, usually cement, retards bacterial activities, changes the pH from acidic to alkaline and reduces moisture content significantly. Changes in solidified peat may be observed physically by measuring unconfined compressive strength (UCS) followed by scanning electron microscopy (SEM). Chemical reactions are quantified using X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), pH and energy-dispersive X-ray (EDX), while biological reactions may be enumerated by bacterial counts and enzymatic activities. Mathematical modelling may be used to elucidate chemical and biological reactions and understand the kinetics of strength improvement. The Michaelis-Menten equation is applicable as enzymes secreted by bacteria in peat dissolve hydration products in solidified peat. Affirmation of the theory used in determining chemical and biological mechanisms is critical in helping geotechnical engineers to choose the best method of peat solidification with minimal environmental impact.

Keywords Peat solidification · Mass balance of peat · Mathematical modelling · Michaelis-Menten equation

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5.1 Introduction

Geotechnical works in peat areas are always a challenge to engineers. Roads or buildings constructed on peat often encounter settlement issues. Peat treatment has been introduced by researchers to harden the peat prior to engineering works. The chemical reaction that strengthens soil particles due to mixing peat with chemical admixtures has not yet been highlighted by geotechnical engineers. The reaction can be elucidated using mathematical modelling and simulation. In this chapter, the nature of peat and possible strengthening agents are discussed before mathematical modelling and simulation are introduced to clarify the chemical reaction that happens during peat treatment work. Awareness may safeguard our environment before work is done on-site; the use of possible chemical pollutants shoud be reduced, and the problem of dissolved transmissible chemical additives used for peat solidification transferred to neibouring areas should be solved or minimised.

5.2 Peat and Its Engineering Challenges

Peat is the cumulative product of decayed plants known as soft soil among geotechnical engineers. Peat contains up to 1800% moisture. According to the nature and management of tropical peat soils (Andriesse 1988), soil consisting of more than 65% organic matter is classified as peat soil. ASTM D 2607–69 (ASTM 1990) states that peat is soil with organic content greater than 75%. Overall, peat can be defined as a brownish or black-coloured soil, depending on the location it is formed and climatic conditions. It is formed by accumulation of decomposed organic matter over thousands of years, under anaerobic conditions. Waterlogging promotes formation. A large amount of porous spaces filled with water makes peat easily compressible. These unique characteristics make construction work on it very challenging to engineers. It is suggested that peat should be treated before any construction work is done.

It is estimated that 4.5% of total land areas or 1 billion acres of land in the world consists of peat. A total area of 25,000 km^2 peat soil in Malaysia is shown in Table 5.1, ranking the country ninth with the biggest total area of peat soil (Mesri and Ajlouni 2007). The characteristics of peat depend on the original plant material, e.g. moss or fern, and the climate of specific locations. In most European countries,

Table 5.1 Peat areas in different countries

No.	Country	Area (km^2)		No.	Country	Area (km^2)
1	Canada	1,500,000		6	Sweden	70,000
2	USSR	1,500,000		7	China	42,000
3	United States	600,000		8	Norway	30,000
4	Indonesia	170,000		9	Malaysia	25,000
5	Finland	100,000		10	Germany	16,000

peat originates from bogs and fens. There is variability in microbial communities of peat. In European regions it is normally wet and records constant or similar moisture content throughout the year. Although peats in temperate regions, with tropical climates, are saturated during wet seasons and of low moisture content in dry seasons, peats are easily ignited and are fire hazards (American Coal Ash Association 2007).

Around 2.4 million hectares of Malaysian land area is covered with tropical peat. Sarawak is the state that has the largest peat area, 69.5% of the total peat area in Malaysia (Mutalib et al. 1992). In peninsular Malaysia, the peat area of Pahang, Perak and Selangor states comprises 17.2% of the total land area (Mesri and Ajlouni 2007).

Peat has a low shear strength of 5–17 kPa when tested using vane shear; it is not a favourable soil for construction work (Hebib and Farell 2003; Wong et al. 2009). One of the reasons for the low strength of peat is its high porosity, affecting all peat types worldwide (Al-Ani et al. 2013). In construction work, there is a minimum strength of soil required before a basement is considered safe; however, no specific guideline has been established for construction in peat areas. The New Zealand Building Code proposed that other types of soil have an ‘allowable bearing’ pressure of 100 kPa before building (New Zealand Building Code Requirements 2011). Building codes of New York City (2008) and New Zealand Building Code (2011) advise a mass stabilisation or vertical piling for construction on peat areas.

As peats are prone to shrinkage and have a very low bearing capacity, they are not suitable for building on (Islam and Hashim 2010). Dramatic peat shrinkage occurs during drier seasons, leaving buildings ‘hanging’ on piling structure or facing settlement issues. The high moisture content of peat effects shrinkage of a few metres beneath the original level during droughts (Holden et al. 2004; Lindsay et al. 2015). When natural organic soils are drained, subsidence caused by consolidation may occur (Van Hardeveld et al. 2017). Perpetually, after the water table is lowered, saturated organic layers are compacted due to a loss of buoyancy (Wösten et al. 1997). When a high negative water pressure occurs due to loss of water, organic materials above water level experience shrinkage and rapid decomposition. Compaction follows decomposition processes when biochemical oxidation takes place (PS Konsultant 1998).

In most countries, peat areas are abandoned as treatment of peat incurs a high cost. However, Brazil, Canada and Denmark take advantage of peat’s natural carbon stock making beneficial products such as peat bricks, peat fuel and supplements for agricultural activity (Peat Society 2015). In Malaysia and in other developed countries such as Sweden, the study of peat treatment has become important. According to Pontian District Municipal Council in a 2014–2018 report, Johor Bahru, Malaysia, (town) has a residential growth of 280% from 2003 to 2013 compared to other peat-based areas in the district with only 10% growth in the same time interval. This highlights the importance of peat treatment to the ministry for the purpose of balanced urbanisation. Knowledge of peat decomposition level is essential as it infers or leads to accurately predict the potential of any physical modification on peat soil (Mohamed et al. 2002). Treatment studies should consider all peat types, to give solutions that suit all peat areas.

Peats originate from organic matter, some of which contains complex aromatic macromolecules known as humic substances that contribute to odour, taste and acidity in water supplies (Fong and Murtedza 2007). The chemical and physical properties of soils involve humic substances, the most chemically active fractions of peat with a high surface area and surface charge (Santagata et al. 2008). Stabilisation may be carried out using the agent ordinary Portland cement (OPC), though hydration processes are interrupted by humic acid, organic matter with a low pH. Stabilisation is disrupted when acid reacts with calcium from cement hydrolysis, resulting in insoluble calcium humic acid, which makes calcium crystallisation a challenging process. Calcium crystallisation products provide the key strengthening of cemented soil (Santagata et al. 2008; Hashim and Islam 2008).

Peat is classified according to its decomposition level. Categories of less decomposed (more than 66% fibre), moderately decomposed (33–66% fibre) and most decomposed (less than 33% fibre) peat are known as fibric, hemic and sapric respectively. The structure of decomposed peat varies in its degree of humification. Physical properties of peat vary with decomposition level. Peat moisture content alone cannot be used to predict decomposition as it changes with location, original vegetation, climate and water table (Rahman and Chan 2013). Abd Rahman (2015) confirms the relationship between peat decomposition level and the solidification process. The amount of fibre in peat determines the amount of filler needed for peat treatment.

The degree of decomposition varies between peat mosses depending on the resistance degree of plants and environmental factors such as the presence of hydrolytic enzymes produced by decomposing microorganisms. Factors affect microbial activity directly and then indirectly on the decomposition process. These include biochemical stability of the peat, water activity, temperature, pH and aeration (Huat 2004). Variations give a wide range of physical properties to peat including colour, texture, density, specific gravity, porosity and pore size, which are all related to the degree of decomposition. Higher decomposition levels of peat lead to a decrease in the particle size of organic matter (Boelter 1968). Microorganisms have more activity with increases in water content and aeration (Wolińska and Stępniewska 2012). Based on the degree of decomposition for each type, fibric peats are rich with organic matter and have a high porosity due to the large pore size, while sapric peats have a small pore size and low organic matter. Figure 5.1 depicts peat layers: The remnants of logs and woody plants can be seen clearly in fibric peat; the remnants of decomposing wood and trunks can also be noted in hemic peat, but both are absent in sapric peat. The decomposition of peat is organised and represents the peat profile, where fibric peat is normally found at the top of the peat soil layer (Abd Rahman 2015).

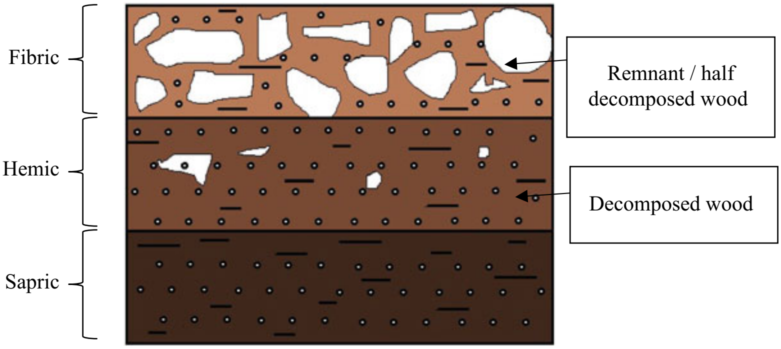

Fig. 5.1 Profile morphology of organic soil

5.3 Peat Solidification Theory

Any soil that is not stable, strong and durable is considered weak and unable to bear high load. Soil solidification, stabilisation or modification is the process of improving the physical and engineering properties of a soil to predetermined targets (Eisazadeh et al. 2010). Soil stabilisation is a solution that increases the bearing capacity and strength of the soil. Stabilisation also refers to the selection of the stabiliser in order to achieve target strengths or stiffness values in addition to modification (Makusa 2012).

The challenge in peat stabilisation is finding the best binder, filler and ratio for the admixture. Several studies on binder and filler for soft soil stabilisation have been conducted, which include the use of recycled waste products, rice husks and many more (Huat 2004). According to Makusa (2012), there are two types of soil stabilisation methods: mechanical and chemical stabilisation. Mechanical stabilising methods include induced vibration or compaction, as well as adding other physical properties like barriers and nails. These are best suited for coarse-grained soils or aggregates at optimum or below optimum moisture contents (Dhakal 2012) and are not suitable for peat soils. Chemical stabilisation, often known as soil stabilisation, is based on a chemical reaction between a stabiliser and the minerals in the soil. There are two groups of chemical stabiliser – traditional and non-traditional. Liu et al. (2011) stated that traditional stabilisers such as cement and lime are more common as compared to non-traditional stabilisers including liquid polymers, silicates and lignin derivatives. This may be due to the cheap price of traditional stabilisers especially if the stabilisation needed to cover a large area is easily obtained. According to Dhakal (2012), clayey soil is the most effective for chemical stabilisation. The selection of stabilisation technique depends on the soil type and its condition.

The water content; the physical, chemical and mineralogical properties of peats; the nature and amount of organic matter included; and the pH of pore water all play a role in peat stabilisation. As different types of peat have their own unique characteristics, no absolute ratio of properties can be used to indicate solidification. The qualities of treated organic soils by binders and fillers are dependent on both the concentration of organic matter and the nature and type of organic matter (Tremblay et al. 2002). The degradation of biodegradable chemicals also affects the strength gained. Fine-grained soils' engineering behaviour is governed by their specific surface area (Santamarina et al. 2002). A study by Kazemian et al. (2009) found that sapric, hemic and fibric peats have specific surface areas of 93, 69 and 50 m^2/g, respectively. On a unit mass or volume basis, as the specific surface of sapric peat increases, more surface area is accessible for reaction. A higher shear strength is obtained in comparison with fibric and hemic peats (Kazemian et al. 2009). In the following subsections, the solidification of peats will be reviewed and evaluated.

5.3.1 Techniques in Peat Solidification

In many soil solidification studies, cement is used as a binder (Tremblay et al. 2002; Consoli et al. 2000; Rotta et al. 2003; Rao and Shivananda 2005; Ahnberg 2006). Cement is a hydraulic binder. A hydraulic binder is self-curing when in contact with water, while a non-hydraulic binder requires a catalyst to initiate curing. A hydraulic binder will stabilise almost any soil. When a binder interacts with soft soil, it creates a substance with greater engineering qualities than the original soil (Hebib and Farell 2003). The finer the grain size of cement, the more reactive it will be (Kazemian et al. 2009).

Cement is commonly used to alleviate soil acidity, as well as to improve the physical condition of the soil (Rotta et al. 2003). The pozzolanic reaction increases the pH of pore water due to dissolution of hydrated lime. The strong base dissolves both soil silica and alumina from soil minerals (Rao and Shivananda 2005). Care must be taken to ensure homogeneous mixing; unlike lime cement does not diffuse into soil mass (Ahnberg 2006). Thermogravimetric analysis (TGA) is often use to determine the presence of $Ca(OH)_2$ in OPC or solidified soil. Weight loss between 450 and 580 °C was used to determine the $Ca(OH)_2$ composition (El-Jazairi and Illston 1977; Wang et al. 2004). The change of cementitious products can be indicated by the change of $Ca(OH)_2$ by hydration process which produces ettringite (Horpibulsuk 2012).

Beside cement, researchers mix peat with a variety of pozzolan materials to enhance secondary reactions and reduce the cement cost. Pozzolan is a material made up of siliceous or siliceous and aluminous materials with little to no cementitious value. Pozzolan reacts chemically with calcium hydroxide at room temperature in the presence of water to generate cementitious compounds (Mehta 1987). Small amounts of secondary pozzolanic materials are added to admixtures to promote secondary pozzolanic reactions. Fly ash is commonly known as a good pozzolan for soil stabilisation (Wongsa et al. 2016).

Sodium silicate is an admixture used in peat solidification studies (Kazemian et al. 2011a, b, c). According to Karol (2003) and the US Army Corps of Engineers (USACE 1995), when sodium silicate solution and an adequate solution of alkali metal salt (sodium and potassium) are mixed, the reaction generates a gel instantly. As the reaction is fast, solutions do not completely contact with each other; unstable interfaces ensure that enough contact occurs to form a continuous gel network that can be followed through stabilised soil. The study by Kazemian et al. (2009) found that sodium silicates can solidify peat and achieve higher strength; more than 50% of the strength is gained when solidifying using OPC in controlled acidic media. The sodium silicates, however, react more in hemic and sapric peats compared to fibric peat.

The ground granulated blast furnace slag (GGBS), calcium oxide (CaO) and sodium bentonite are among secondary pozzolans that are used in peat. These admixtures are good binders with cement. Most secondary pozzolans cannot achieve significant strength without cement as no hydrolysis takes place; no ettringite is formed to bind the soil particles. Combinations of GGBS and cement lengthen the curing effect as it is reactive for long durations (after years). The mixture was found to be efficient in gaining strength in peat solidification studies (Axelsson et al. 2002; Mass Stabilization Manual 2005). Calcium oxide, on the other hand, works differently. Calcium oxide reacts well with water to produce slake lime. Slake lime is very reactive to carbon dioxide, producing mortar. Mortar is a paste that gradually hardens and cements bricks together. The use of calcium oxide in soil treatment is limited to the soil natural water content; however, in the case of peat, a high water content enables mortar formation when calcium oxide is used.

5.3.2 *Stabilisation of Peat by Cement*

Organic soils have been shown to slow or prohibit the hydration of binders such as cement in binder-soil mixes (Hebib and Farell 2003). With a high organic content and less solid particles in peat, cement alone as a chemical admixture is insufficient to provide peat stabilisation. Peat has a significantly lower content of clay particles that enter secondary pozzolanic reactions than clay and silt (Janz and Johansson 2002). As such, the interaction between hydrated lime Ca(OH) and the soil is less effective in secondary pozzolanic reactions. Unless a sufficient amount of cement is put to the soil, peat stabilisation by cement will not lead to a significant increase in strength. A study by Ahnberg et al. (1995) found that peat achieves the lowest shear strength with cement stabilisation compared to other types of soil. Similarly, with the highest water/cement ratio (wcr), cement-stabilised peat demonstrated the lowest shear strength compared to other types of soil (Ahnberg et al. 1995). Evidence from both figures shows that less solid particles and high organic matter make peat soil porous and spongy in nature; the organic matter tends to impede the hydration of cement when it is used to stabilise soil (Wolińska and Stępniewska 2012).

Abd Rahman (2015) discusses the concept of natural water content in peat. As peat is naturally acidic, containing humic acid, the concept of water consumption in peat solidification is varied. Water in the peat increases after neutralisation of humic acid takes place. The neutralisation produces water, which will react with OPC to form ettringite. Neutralisation is a process involving a reaction between acid and alkaline, producing water and salt as shown in Eq. (5.1).

$$\text{Acid} + \text{Alkaline} \rightarrow \text{Water} + \text{Salt} \tag{5.1}$$

Neutralisation can be detected by pH 7 of a mixture and an increasing amount of water as the result of combination of the aqueous solution from both acid and alkaline. An exact quantity of acid and base (OH^- ion) is needed to achieve neutralisation. Exceeding the neutralisation limit by any of the elements causes the material to be dominant by the respective element, either acid or base. The pH of solidified peats was found to be alkaline (Fig. 5.6). OH^- ions contained in the alkaline binder dominate the pH mixture. The pH value is determined based on the number of OH^- ions present in the solution.

The pH of Pontian peat is around 3–4 and represents the high number of H^+ ions in humic acid (Abd Rahman 2015). Humic acid is a weak acid; direct exposure to peat does not give irritation or corrosion. Moisture in peat contains an aqueous humic acid. Since ettringite is formed by the interaction between cement and water, neutralisation does not occur in a mixture of solidified peat. The amount of water present in the mixture depends on the neutralisation process. Studies by Ali et al. (2010), Akol (2012), Wong et al. (2013a, b) and Abd Rahman (2015) show that peat is acidic by nature, while solidified peat is alkaline with a pH range from 8.83 to 12.11 (Fig. 5.2). The alkaline condition is important for the reaction between OPC and water, interlocking the hydration product and soil particles.

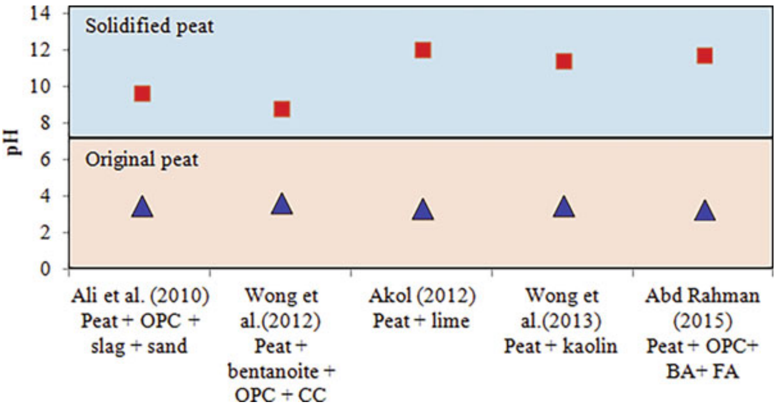

Fig. 5.2 pH of peat and solidified peat. **CC* calcium carbonate, *OPC* ordinary Portland cement, *BA* bottom ash, *FA* fly ash

The presence of black humic acid and fulvic acid in peat soil makes cementation and hardening of peat-cement admixtures difficult. Wherever calcium is present in solution, black humic acid interacts with it to generate insoluble calcium humic acid (Rahman and Chan 2013). Calcium crystallisation is hard due to the combination of humic acid and calcium ions created during cement hydration; yet, crystallisation increases the strength of the peat soil-cement mixture (Rahman and Chan 2013). Exposure of cement to fulvic acid solutions generates the hydration of cement. The chemical reaction between fulvic acid and cement minerals results in an absorbed layer, which obstructs the hydration process. Furthermore, existing crystals such as calcium aluminate hydrate, calcium sulfate-aluminate hydrate and calcium ferrite-aluminate hydrate are decomposed by fulvic acid, inhibiting the creation of a soil-cement structure (Rahman and Chan 2013). The acids lower the pH of the soil, which has an adverse effect on the binder's reaction rate, resulting in a slower strength gain in the peat (Axelsson et al. 2002).

Organic acids, when mixed with soil and cement, generate a pH lower than 9 in porous solutions, preventing the creation of cementing products because the pH has become too low to support secondary mineral formation (Liu et al. 2011). The process of soil stabilisation will be slowed unless a large amount of cement is mixed with the soil to neutralise the acids. It is uneconomical to add a big amount of cement to the soil to improve peat ground. As a result, it is obvious that the physico-chemical reactions that occur, such as cement hydration and hardening, as well as interactions between components in the soil and cement hydration products, are responsible for the increased strength of cement-stabilised soil (Abd Rahman 2015).

Excessive organic matter in peat effects a high water retention capacity, and organic particles on the surface of cement and solid soil particles absorb water during cement hydrolysis in the soil. Both the development of cement hydration products and the hydration of solid soil particles and hydration products are hampered by this (Abd Rahman 2015). As a result, only limited increments can be achieved in peat-cement admixture strength. This was evident when Chen and Wang (2006) mentioned that the strength of peat did not reach 300 kPa with deep mixing with a cement ratio of up to 30%, in a foundation reinforcing project on peat undertaken in 1985. A clear understanding on the behaviour of organic matter in the process of stabilisation of peat by suitable chemical admixtures is vital in order to outline effective peat stabilisation.

5.3.3 Effect of Pozzolan as a Secondary Additive in Peat Stabilisation

To increase the secondary pozzolanic reaction in the stabilised soil, small amounts of pozzolans such as kaolinite, sodium bentonite and fly ash can be added to the cement-stabilised peat (Torkittikul et al. 2017). Under specific conditions, both cement and pozzolan used for peat stabilisation react with water in the soil to generate a high-strength product that binds soil particles together. However, the ratio of lime to silica ($Ca(OH)_2:SiO_2$) affects reactivity. The material is more hydraulic if the ratio is higher (Janz and Johansson 2002).

5.4 Gaps in Peat Improvement Studies

It can be concluded that the effectiveness and dosage of binder type on the stabilisation of peat are site specific since the properties of peat differ geographically. Different types of peat react with different types of binder at certain binder dosage to achieve effective stabilisation. The unconfined compressive strength gain of stabilised soil rose with an increase in binder dosage, filler and curing time, according to a review of numerous experimental examinations of stabilised peat. Abd Rahman (2015) shows that peat strength can be improved. However, two patterns manifest during stabilisation effecting optimum and non-optimum mixtures during the treatment process (Fig. 5.3). The same pattern was detected by Kido et al. (2009), Kalantari et al. (2013) and Huat et al. (2014) where the peat was of less strength after a certain curing period. Most studies stop at this engineering finding. The chemical reaction, other than hydration, is expected to be the main cause of peat solidification. The alteration of the chemical bond in solidified peat may lead to a new product, potentially a more cost-effective and efficient solution.

The role of the microbial community in peat decomposition of plants has not been considered. Researchers estimate that microbial activity is frozen during the stabilisation process. However, current research in concrete studies introduces self-healing concrete, where microbes are used to react with chemicals from concrete to self-paste the leaking concrete. The concrete research used $CaCO_3$, the main element found in OPC.

5.5 Biological Reaction in Peat Solidification

5.5.1 Microbes in Peat

Microorganisms are responsible for the decomposition of plants in peat. Edaphic communities are varied and comprised of bacteria, actinomycetes, fungi, algae and protozoa. Peat lands contain large microbial populations of a wide metabolic diversity (Williams and Crawford 1983). Studies by Kraigher et al. (2006) and Ausec et al. (2009) explore relationships in microbial activity and structure in two fens and one bog. The result from the studies shows that from the 16S rRNA genes, *Proteobacteria* and *Acidobacteria* dominate fen and bog soils (Thrash and Coates 2011). However, bog and fen soils show a clear distinction in their bacterial communities despite sharing dominant phyla. A significant difference can be

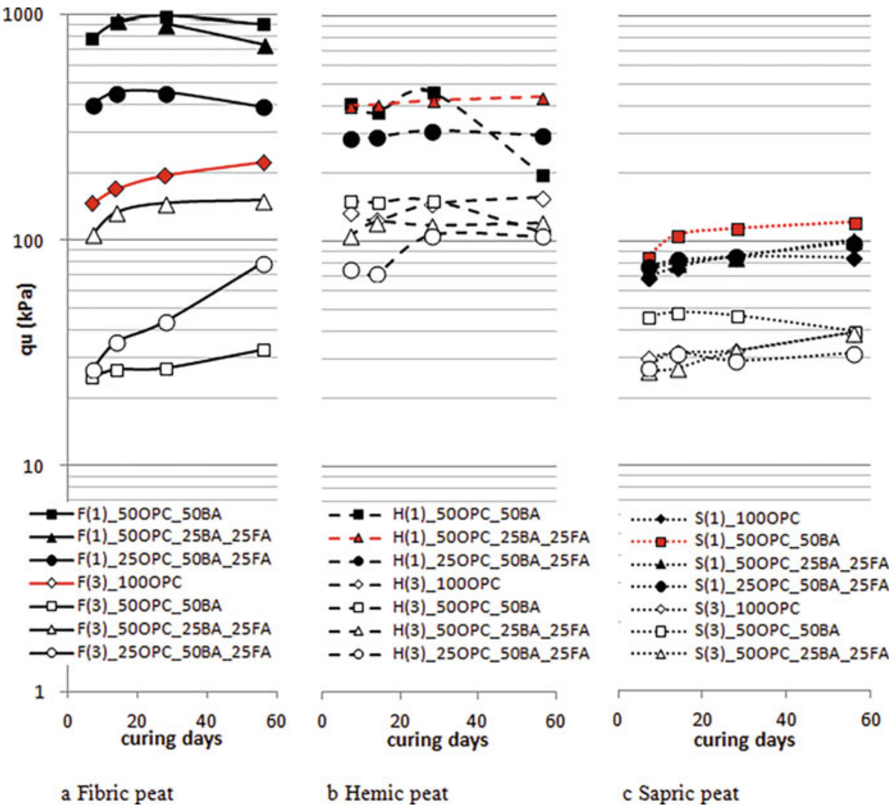

Fig. 5.3 Strength (q_u) versus curing days (Abd Rahman 2015). This infers a potential reaction between microbes and solidified peats. *Red lines indicate optimum mixture

observed at the level of relative abundance of species affiliated with the phylum *Acidobacteria*, 23% in the fen and 40% in the bog gene library respectively.

The types of vegetation from which peat originates cause differences in microbial community makeup. Ombrotrophic bogs are made up of slow-decomposing mosses and shrubs that get their nutrients from both dry and wet deposition (Aerts et al. 1999). Minerotrophic fens, on the other hand, are made up of more easily decomposable sedges, plants and shrubs that get their nutrients from groundwater (Bragazza et al. 2007). According to Tamburini et al. (2017), microorganisms using degraded cellulose by a depolymerisation step allow a metabolisation step. Table 5.2 lists the variety of microbes found in different regions of peat.

All microbes have unique characteristics; some are pathogenic and can be harmful to people. The microbes in Pontian peat may be different from peat from Europe countries as studied by Liimatainen et al. (2018), Novak et al. (2018) and Lorenz and Lal (2018).

Table 5.2 Variety of microbes found in different regions of peat

Microbe	Location	Vegetation	Reference
Arthrobacter, *Bacillus* spp.	Riviere-du-Loup, Quebec, Canada	Finnish *Sphagnum*	Boehm et al. (1993)
Bacillus acidicola ssp. Nov	Wisconsin, USA	Not reported	Albert et al. (2005)
Rhizobium, *Agrobacterium*, *Acidobacteria*	Latvia, Denmark and Ireland	Not reported	Hunter et al. (2007)
Proteobacteria, *Acidobacteria*	Ljubljana, Slovenia	*Sphagnum* sp. *Arrhenatherum elatius*, *Dactylis glomerata*, *Festuca rubra*, *Equisetum palustre*, *Galium mollugo*, *Ranunculus repens*, *Achillea millefolium*, *Leucanthemum ircutianum* and *Centaurea jacea*	Mandic-Mulec et al. (2014)
Actinobacteria, *Bacteroidetes*	Svalbard	Not reported	Žifčáková et al. (2016)
Acidobacteria	Xistral Mountains (Northwestern Spain)	*Sphagnum subnitens* Russ & Warnst., *Molinia caerulea* (L.), *Carex duriaeui* Steud. ex Kunze, *Agrostis stolonifera* L. and *A. curtisii* Kerguélen., *Potentilla erecta* (L.), *Erica mackaiana* Bab., *Deschampsia flexuosa* (L.), *Carex panicea* L. and *Calluna vulgaris* (L.), *Eriophorum angustifolium*	Guanlin et al. (2017)
Thiobacillus	Finland	Not mentioned	Hartikainen et al. (2002)
Burkholderia gladioli	Riau, Indonesia	Not mentioned	Istina et al. (2015)
Methanotrophs	Not mentioned	*Sphagnum* mosses	Kip et al. (2010)
B. phenazinium	Germany	Not mentioned	Al-Sadi et al. (2016)

5.5.2 *Microbes in Solidified Soil*

The study of microbes in solidified soil has attracted interest since the last turn of the century. Most studies focus on utilising bacteria in soil treatment (Ivanov and Chu 2008; Kim et al. 2013; Abo-El-Enein 2013; Ismail et al. 2014; Ng et al. 2012). The biocementation concept where microbes and cement are mixed to form a cementation product lessens the void in soil. The bioclogging process was introduced by Ng et al. (2012) where the soil void is filled by microbial-induced biochemical products. In the study, Ng et al. (2012) concentrate used uratic bacteria that are naturally found to produce a cemantitious product. Urase activity was found to increase rapidly in mediums with pH 6–8.

In a study by Ivarson (1977), it was shown that the number of microbes in surface peat (normally fibric peat) was higher compared to those from subsurface (hemic peat) and subsoil (sapric peat). It was recorded that fibric and hemic types have microbe counts of 25×10^5 CFU/g and 5×10^5 CFU/g, respectively. However, when lime was introduced to peat, the number of microbes increased dramatically to 6540×10^5 CFU/g for fibric peat and 2940×10^5 CFU/g for hemic peat. This leads to biocementation where the lime content from cement can be expected to stimulate the microbes in peat.

Ivanov and Chu (2008) investigated the potential of biocementation, which is described as a method that uses microbial activity or products to improve the strength and stiffness properties of soils and rocks. Ivanov and Chu (2008), however, limit their research to clay and sand only. Kucharski et al. (2005) filed a patent application for microbial biocementation, which involves combining a permeable material with a biomass of urease-producing microbes, urea and soluble calcium salts to make a high-strength cement. Microorganisms enable rapid urea hydrolysis, raise pH during urea-to-ammonia hydrolysis and create calcite in soils and rocks. Compressive strength of the cement produced was up to 5 MPa. Conglomerate, breccia, sandstone, siltstone, shale, limestone, gypsum, peat, lignite, sand, soil, clay, sediments and sawdust are among the materials treated by biocementation. *Bacillus*, *Sporosarcina*, *Sporolactobacillus*, *Clostridium* and *Desulfotomaculum* are among the urease-producing bacteria used in the study (Ivanov and Chu 2008).

The process of producing urease for the hydrolysis of urea $CO\ (NH_2)_2$ into carbonate ($CO_3{}^{2-}$) and ammonium ($NH_4{}^{+}$) is as follows (Karthik and Rao 2016):

$$
\begin{aligned}
&CO(NH_2)_2 + H_2O \rightarrow NH_2\ COOH + NH3\\
&NH_2\ COOH + H_2O \rightarrow NH_3 + H_2CO_3\\
&H_2CO_3 \rightarrow HCO_3{}^{-} + H^{+}\\
&2\ NH_3 + 2\ H_2O \rightarrow 2\ NH_4{}^{+} + 2\ OH^{-}\\
&H\ CO_3{}^{-} + H^{+} + 2\ NH_4{}^{+} + 2\ OH^{-} \rightarrow CO_3{}^{2-} + 2\ NH_4{}^{-} + 2\ H_2O
\end{aligned}
$$

These reactions increase the pH and form carbonate ions (Ramakrishnan et al. 1998).

5.5.3 *Microbes in Cement Study*

Recent trends in concrete or cement studies utilise microbes to develop self-healing concrete. Basically, microbes are known to have unique characteristics which are vulnerable to environmental changes. However, microbes can survive in extreme conditions. The process of self-healing concrete requires adding microbes to the cement before pouring it into the concrete material. In crack-sealing, bacterial concrete is formed via the metabolic conversion of calcium lactate to calcium carbonate (Jonkers et al. 2010; Kim et al. 2013). Whenever cracking occurs in concrete, rainwater fills the crack, stimulating the inserted microbe and reactivating it to produce more carbon dioxide. The carbon dioxide reacts with calcium lactate and produces calcium carbonate which hardens the material (Jonkers 2011). Ismail et al. (2014) and Pradeep Kumar et al. (2015) have confirmed the success of this hypothesis. Small cracking was found to take about 100 days to recover (Joshi et al. 2017). *Bacillus* spp. work well with cement and are easily obtained in the soil (Ivanov and Chu 2008; Jonkers 2011). Table 5.3 summarises the bacteria that have been used in concrete studies.

Table 5.3 Summary of bacteria used in concrete studies

Bacteria and products	Findings	References
Escherichia coli; *Shewanella*	Mortar specimens induced with *Shewanella* show an increase in strength. The growth of fibres within the pores was observed under SEM and supported strength in increments.	Ghosh et al. (2005)
Bacillus sphaericus	SEM showed the presence of carbonate crystals on the mortar surface.	De Muynck et al. (2008)
EM product	The reaction of bacteria with cement was not well explained. Compressive strength increased in concrete specimens. No microstructural examination reported.	Jamaludin et al. (2009)
Shewanella	Bacteria mortar shown is different compared to control specimens without bacteria when analysed using environmental scanning electron microscopy (ESEM). XRD analysis confirmed the formation of silicates in the mortar containing bacteria.	Ghosh et al. (2009)
EM product EM ceramic	Mechanism of cement hydration was not explained due to bacterial activity. Compressive strength increased by an average of 28% in EM concrete. SEM was used to examine corrosion due to bacteria.	Bang et al. (2010)
Bacillus pseudofirmus; *Bacillus cohnii*	Bacterial spores were observed using ESEM when *Bacillus pseudofirmus* and *Bacillus cohnii* were isolated in cement stone specimens.	Jonkers et al. (2010)
Bacillus subtilis	The presence of silica and the peak of the quartz were detected using XRD analysis.	Afifudin et al. (2011)
Sporosarcina pasteurii	SEM showed the presence of crystalline calcium carbonate associated in microbed concrete containing silica fume. XRD and EDX results confirmed the presence of calcite with results of high amounts of calcium.	Chahal et al. (2012)
Alkalophilic species	SEM and EDS results indicated the peak of calcite in microbially induced precipitated microbed cement containing sandstones as aggregate. SEM micrograph showed the bottom region is denser than the top region.	Rong et al. (2012)

(continued)

Table 5.3 (continued)

Bacteria and products	Findings	References
EM product	Compressive strength and indirect tensile strength increased in concrete specimens. However, flexural strength results are similar to control specimens. No microstructural examination and chemical phases reported. Confirmed the presence of silica and quartz detected using XRD analysis.	Andrew et al. (2012)
Sporosarcina pasteurii *Bacillus sphaericus*	SEM featured the calcium carbonate precipitated on the surface of microbed normal and lightweight concrete. Calcite crystals with little vaterite crystals for both types of bacteria were indicated in XRD pattern.	Kim et al. (2013)
Sporosarcina pasteurii	SEM with energy-dispersive X-ray analyser (EDAX) depicts that $CaC0_3$ is precipitated within the cement mortar matrix. XRD was not used to quantify the minerals.	Abo-El-Enein (2013)
Effective microorganism (EM)	Compressive strength improved with curing days and amount of microbes. SEM micrograph of microbed cement paste had less voids and was denser compared to control cement paste.	Ismail et al. (2014)

Since microbes were reported to be part of the solidification product, microbes present in peat may work the same in solidified peat. However, no successful biocementation field applications have been reported.

5.6 Chemical Reactions in Peat Solidification

5.6.1 *Chemical Bonding/Sketching for Raw Peat*

The chemical bonding of all materials is known as a fingerprint of a substance. Different materials have unique molecular structure. Peat in particular is very dynamic. It consists of several types of plant origin and has different decomposition levels, a wide range of acidity and microbial presence. These parameters have limited the sketching of chemical bonds in peat. A general sketching for peat according to its functional group was introduced by Koch (1982) as seen in Fig. 5.4. In 1993, Yonebayashi et al. (1994a, b) used nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy to locate the functional group of peat. However, Yonebayashi et al. (1994a, b) were unable to sketch the molecular structure of the peat, there was no absolute chain in peat from all three sampling locations and the C/N ratio was unstable. Stevenson (1994) has sketched the molecular bonding of humic acid, a typical acid present in peat soil (Fig. 5.5).

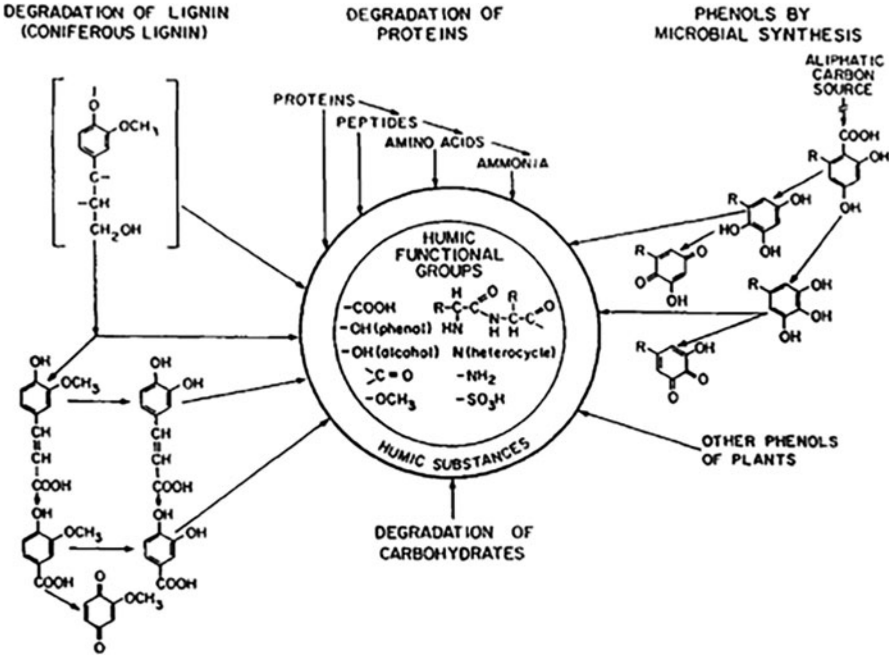

Fig. 5.4 Degradation of plant residues and the formation of humic substances in peat. (Koch 1982)

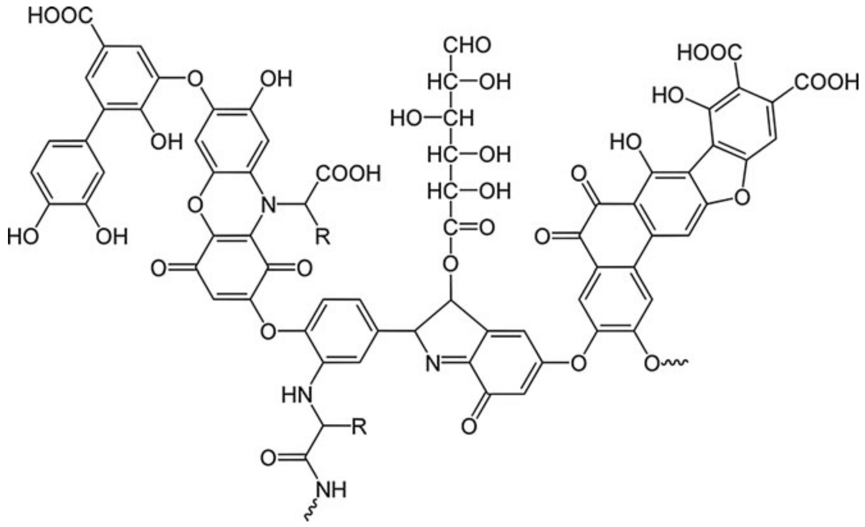

Fig. 5.5 A typical humic acid with a range of components such as quinone, phenol, catechol and sugar moieties in peat. (Yonebayashi et al. 1994a, b)

5.6.2 *Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) and X-Ray Diffraction (XRD) Analysis Explain Chemical Alteration in Peat*

FTIR and XRD are used in determining the chemical and mineral elements in samples. FTIR determines the absorbance of infrared rays in a sample. Different functional groups will give different absorbance values and normally read in ranges. XRD works by determining minerals in samples by dispersing X-rays. The combination of information gained by both FTIR and XRD could be utilised to obtain the chemical sketching of specific peat samples. Yonebayashi et al. (1994a, b) examined the occurrence of carboxyl, carbonyl, phenolic hydroxyl and alcoholic hydroxyl groups in humic acids. It has been shown that the amount of lignin and cellulose decreases with increasing humic acid in peat. Yonebayashi et al. (1994a, b) used NMR to classify the chemical in the sample. It was concluded that humic acids from tropical peat have long aliphatic chains due to the origin of their plant source.

Kyziol (2002) used FTIR to determine functional groups in peat from three different locations. Peat from different sites has the same functional group at wavelength 2900, 2780, 2350, 1480 cm^{-1} and more minor peaks in the range 800–1300 cm^{-1} (Fig. 5.6). Table 5.4 summarises the techniques used to consider chemical bonding.

5.6.3 *Chemical Reaction Models of Peat Processes*

To model chemical reactions that take place in peat solidification, an understanding of the concept of chemical reaction is essential. The kinetics behind chemical reactions are influenced by the rate of reaction, reversible or non-reversible reaction, rate constant, reaction order and reaction mechanism.

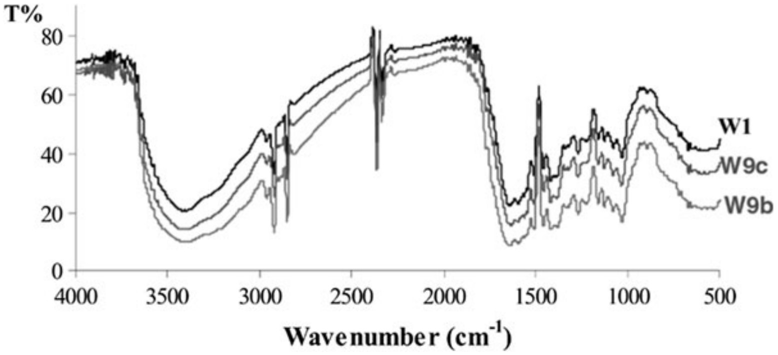

Fig. 5.6 FTIR spectra of selected peats. (Kyziol 2002). W1 Alder Peat Humus, W9b Brushwood Peat Humus, W9c Rush (Reed-Sedge) Peat

Table 5.4 Techniques used to determine chemical bonding in peat

References	Technique used	Findings
Yonebayashi et al. (1994a, b)	Proton NMR spectra	The atomic ratios of C, H, N and H/C in tropical peat humic acids ranged from 54% to 63%, 4.5% to 7.1%, 1.1% to 3.9% and 0.96% to 1.35%, respectively
		Humic acids from tropical peats have concentrations of carboxyl, carbonyl, phenolic hydroxyl and alcoholic hydroxyl groups ranging from 3.1 to 5.1, 1.0 to 5.3, 0.03 to 1.1 and 3.1 to 23.5 mol kg^{-1}, respectively
		The methoxyl group, lactone ring and aromatic ring proton percentages of tropical peat humic acids ranged from 16% to 57%, 6% to 41% and 4% to 17%, respectively
		The percentages of aliphatic protons linked to carbon atoms, fJ to aromatic rings and terminal methyl protons were 1–6, 13–39 and 4–14%, respectively
Kyziol (2002)	Functional group – FTIR	Product of humification process of organic matter has similar chemical structure when compared with other peat samples from different regions
Romão et al. (2007)	XRD	Peat samples give an amorphous pattern which indicates no presence of absolute mineral in peat

The reaction mechanism of materials takes place via adsorption, desorption and surface reaction. These reactions are spurred by temperature, pressure and biological elements. All parameters mentioned must be considered when modelling the chemical reaction of a material. There are chemical reaction models which use conventional equations or mathematical models using software in explaining the reaction that takes place in particular samples.

As peat is derived from plant materials and affected by microbial activity, a biochemical reaction model is suitable for clarifying the reaction inside the solidified peat. The majority of soil biochemical reactions take place in organic dominated layers (McLaren and Peterson 1967). Table 5.5 summarises modelling and simulation of chemical reactions as discussed by Higham (2008).

5.6.4 Chemical Reactions Behind Soil Improvements

Eisazadeh et al. (2012) used NMR and FTIR techniques to analyse the functional group and local bonding of lime-treated soil. The study treated green bentonite and laterite soil (rich with iron) by using lime in various ratios and curing periods. As bentonite and laterite soils are rich with minerals, changes in clay minerals were expected. Conversely, the silica in quartz was found not to be affected by the presence of lime. The study on the effect of curing period of treated clay found a promising strengthening effect for all types of mixing up to 8 months of curing. However, the NMR and FTIR analysis for all mixing portions and curing periods did

Table 5.5 Summary of mathematical modelling and simulations of chemical reaction

Model/ simulation	Explanation	Relation with solidified peat study
Michaelis-Menten equation	Associate with a system involving four species: 1. A substrate, S_1 2. An enzyme, S_2 3. A complex, S_3 4. A product, S_4 $S_1 + S_2 \overset{c_1}{\rightarrow} S_3,$ $S_3 \overset{c_2}{\rightarrow} S_1 + S_2,$ $S_3 \overset{c_3}{\rightarrow} S_4 + S_2.$	Microbes in peat secrete enzyme that will eventually react with chemical additives and peat soil itself
	Expectation: 1. Reaction happens when $S1$ molecules meet $S2$ molecules. 2. c_1 is a scaling factor that takes into account the fact that not all collisions result in a reaction, 3. Two molecules from the same chemical species interact.	
	$\frac{dP(\mathrm{x},t)}{dt} = \sum_{j=1}^{M} \left(a_j(\mathrm{x} - v_j)P(\mathrm{x} - v_j, t) - a_j(\mathrm{x})P(\mathrm{x},t)\right).$ For probability that a happens, happens j is a certain vector	
Stochastic simulation algorithm (SSA)	Rather than computing the complete probability distribution, single realisations of the state vector are computed $p(\tau, j \mid \mathrm{x}, t) = \frac{a_j(\mathrm{x})}{a_{\mathrm{sum}}(\mathrm{x})} a_{\mathrm{sum}}(\mathrm{x}) e^{-a_{\mathrm{sum}(\mathrm{x})\tau}}.$ Depending on the next reaction index and time for next reaction	Assumption of reaction rate can be calculated using an algorithm; however, as peat is complex, single algorithms are expected to be insufficient, and so must be applied in sequence pending variations
Tau-leaping	$\mathrm{X}(t+\tau) = \mathrm{X}(t) + \sum_{j=1}^{M} v_j \mathcal{P}_j\left(a_j(\mathrm{X}(t)), \tau\right),$ To advance SSA. Applicable when τ is sufficiently small that relatively few reactions take place	When peat solidification takes place, lots of reaction step are expected. The mixture of peat and cement itself is exorthermal
Chemical Langevin equation	$\mathrm{Y}(t+\tau) = \mathrm{Y}(t) + \tau \sum_{j=1}^{M} v_j a_j(\mathrm{Y}(t)) + \sqrt{\tau} \sum_{j=1}^{M} v_j \sqrt{a_j(\mathrm{Y}(t))} Z_j.$ Using real values and can do a large number of iterations. Knowledge of a large number of molecules present in the reaction is needed	The possibility in using this model in interpreting the reaction during solidification is there since complex molecule is expected

not reveal any new element in the mixtures. Comparison between non-treated clay and treated clay differed with a new peak identified as a Ca-OH bond. Ca-OH is a functional group of lime. No new element was found in the treated clay that can explain the strengthening effect gained. According to Eisazadeh et al. (2012), lime treatment did not result in significant changes in functional groups in the soil structure component. The pozzolanic reaction expected happened over the curing period though it was not clearly resolved using FTIR and NMR.

Clay soil is known for its homogeneity in size, pores and retained controllable water. However, peat compounds contain several functional groups, and its chemical structure is hard to be visualised; chemical changes in peat are complex to explore and explain.

5.7 Case Study in Pontian, Johor, Malaysia

A case study was carried out in Pontian, Johor, Malaysia where three types of peat – fibric, hemic and sapric – were sampled, solidified and tested for strength (q_u), bacterial count and crystallite (using XRD) for curing in 7, 14, 28 and 56 days. Two mixing formulations were used following Rahman et al. (2015) for the two patterns of strengthening effects owned by solidified peat. Table 5.7 shows the mixed design for both formulations. This differentiates the chemical and biological reactions that happen when samples steadily increase in strength over the curing period (Mixing 1, M1) and samples that show increase in strength for curing days 7, 14 and 28 while decreasing its strength on day 56 (Mixing 2, M2).

Figures 5.7 and 5.8 show the pattern of bacterial counts and the strength of solidified peat over the curing period for both M1 and M2. In M1 bacteria are depleted but remain present in solidified peat; the depleted colony bears a strong relation with the strength. The stronger the solidified peat, the least bacteria count recorded and vice versa.

The finding from XRD showed that the amount of crystallite formed in solidified peat related with the strength of the sample (Fig. 5.9). The samples were found to be stronger when more crystallite formed and vice versa. The dominant crystal present in all samples was identified as pargasite ($NaCa_2[Mg_4Al](Si_6Al_2)O_{22}(OH)_2$) which

Table 5.7 Mixed design for solidified peat (Rahman et al. 2015)

	Fibric peat	Hemic peat	Sapric peat
Mixing 1	OPC with equal amount of dry peat FA 25% Addition of BA to give the coarse particle 23–34% of the total mixtures		
Mixing 2	w/b = 1 50% OPC 25% BA 25% FA	w/b = 3 50% OPC 50% BA	w/b = 3 50% OPC 50% BA

w/b water-to-binder ratio, *FA* fly ash, *BA* bottom ash, *OPC* ordinary Portland cement.

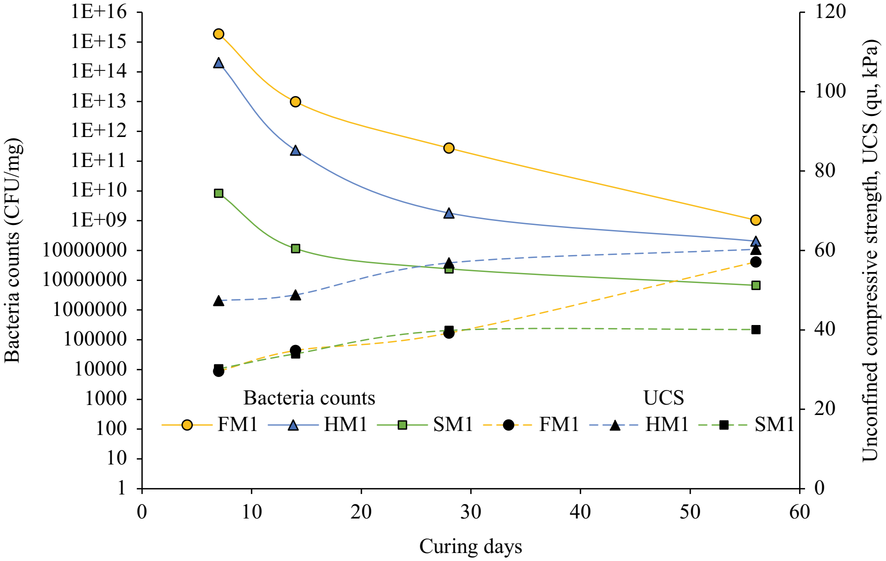

Fig. 5.7 Pattern of bacteria colony in peat and UCS – Mixing 1

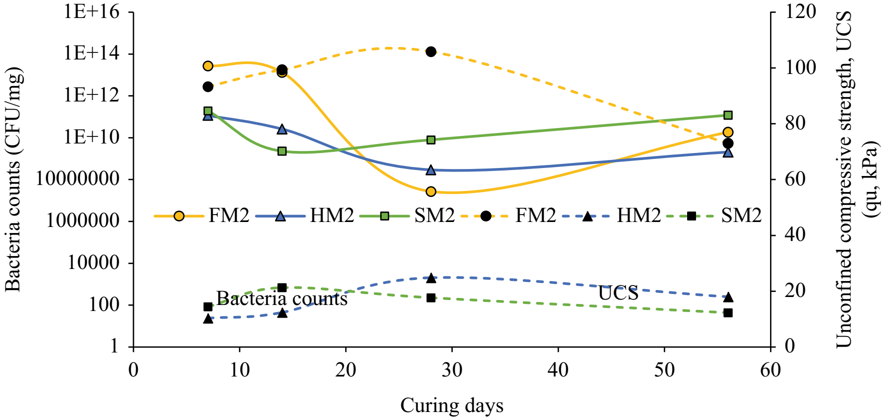

Fig. 5.8 Pattern of bacteria colony in peat and UCS – Mixing 2

has similar physical characteristics with ettringite ($Ca_6Al_2[(SO4)_3(OH)_{12}]$•(24 + 2) H_2O) that is normally found in solidified clay as a result of hydration processes.

The bacteria in this case study were identified as *Bacillus* sp. and were tested using cellulose agar. This medium allows bacteria secreting the enzyme cellulose to grow. The cellulose was monitored using Congo red, and bacterial activity was recorded, as shown in Table 5.8.

Peat solidification work highlights the formation of crystallite as the product of reaction between OPC, bottom ash (BA), fly ash (FA) and acidic peat. Since bacteria

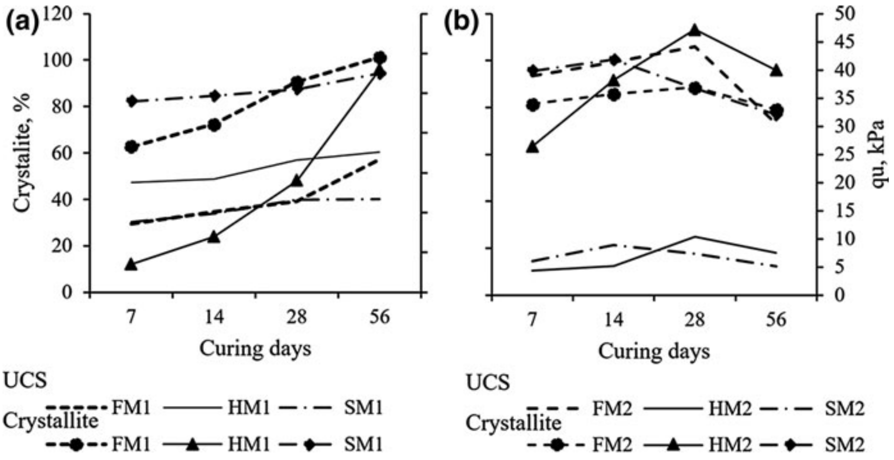

Fig. 5.9 Pattern of strength and percentage of crystallite formed over curing period for solidified peat using M1 and M2 formulations. (**a**) Strength and percentage of crystallite formed increase over curing period of solidified peat for Mixing 1. (**b**) Strength and percentage of crystallite formed increase for D7 and D14 but decrease on D28 and D56 for Mixing 2

Table 5.8 Enzyme activities in peat solidification study

		FM1	HM1	SM1	FM2	HM2	SM2
Halo zone	D7	–	++	++	+	+	+
	D14	–	++	++	–	–	+
	D28	–	++	+	–	–	–
	D56	–	+	–	+	+	+

Negative (–), positive (+), high production (++)

is abundantly present in the peat, the solidification work was not an absolute success as the enzyme secreted by the bacteria was found to dissolve the crystallite formed in M2. This phenomenon may be described using the Michaelis-Menten equation and was used by Cordero et al. (2019) and Sihi et al. (2019) to describe soil enzyme activity.

$$\underset{\text{(a substrate)}}{\text{Crystallite}} + \underset{\text{(an enzyme)}}{\text{cellulase}} \rightarrow \underset{\text{(a complex)}}{\text{weak solidified peat}}$$

$$\left(\mathrm{NaCa_2[Mg_4Al](Si_6Al_2)O_{22}(OH)_2}\right) + \text{cellulase} \rightarrow \text{breakdown of } = \mathrm{O} \text{ and } - \mathrm{OH^-}$$

This finding helps engineers to understand the nature of peat before construction work. It contributes to environmental sustainability by limiting the trial and error during road and basement installation work.

5.8 Conclusion

It can be concluded that the effectiveness and dosage of binder type on the stabilisation of peat are site specific since the properties of peat differ from site to site. Furthermore, different types of peat react with different types of binder at certain binder dosage to achieve effective stabilisation. The unconfined compressive strength gain of the stabilised soil rose with an increase in binder dosage, filler and curing time, according to a review of numerous experimental examinations of stabilised peat. Most studies stop at this engineering finding with little knowledge exploration of cement hydration theory. The chemical reaction other than hydration theory is expected to be the main reason of peat solidification. The alteration of the chemical bond in solidified peat may lead to a new product finding with more cost-effective and cost-efficient solution.

Although it was previously estimated that microbial activity in peat is frozen during the stabilisation process, current research in concrete studies introduce self-healing concrete where microbes are used to react with chemicals from concrete to self-paste the leaking concrete. The concrete research used $CaCO_3$, the main element also found in OPC. This leads to a reaction between microbes and solidified peat being likely. The Michaelis-Menten equation was found to fit well with peat solidification work. Computational modelling may be developed beyond singular stochastic algorithms. Finally, different types of admixture could be proposed to find the pattern of enzymes reacting with induced chemicals in solidification. The study and nature of microbial activity in peat processes and its optimisation may well prove useful in use and transformation of land resources far into the future.

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