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Geochemistry characterisation of marine clay

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Abstract - In evaluating a suitable type of stabiliser, investigating geochemical characteristics is important for improving the properties of soil. This paper assessed the geochemistry of marine clay samples collected from Batu Pahat, Johor, Malaysia. The parameters investigated were pH, loss on ignition (LOI) and the quantities of sulphate, chloride, nitrate and carbonate ions. The results revealed that the clay was an acidic soil with pH of 3.25 and containing 8% of organic matter. The clay also contained 6,071 mg/l, 281 mg/l and 22 mg/l of sulphate, chloride and nitrate ions, respectively. Sulphate and chloride ions from acid rain and decomposed organic matters are the leading causes of acidity found in clay. Further investigation of the physical properties of the soil further indicated that it belonged to a group of clay having high plasticity (CH) and is unsuitable for construction purposes in its natural condition. The concentration of sulphate ions in the clay sample also advocated that the soil is not suitable to be stabilised using cement or lime due to the risk of the formation of a complex compound of calcium sulphoaluminate hydrate (ettringite). Additionally, the sulphate in the marine clay is likely to attack the concrete of the foundation of future infrastructures that may be built in the study area.

1. Introduction

The improvement of physical and engineering properties of weak soils during the development of infrastructures using chemical stabilisation have received significant attention in the literature. Cement and lime are amongst the most commonly used stabilising materials that have been proven to improve the strength of marine clay [1–6]. Although, marine clay found in some areas may require special attention in selecting a suitable stabiliser. The necessity of carefully choosing a stabiliser results once a soil exhibits unusual geochemical properties, (i.e. being highly acidic or with the presence of sulphate ions) [7,8].

Soil pH is the measure of hydrogen ions concentration in the solution of the soil. A logarithmic scale between 1 and 14 measures the pH, with 1, 7 and 14 representing very acidic, neutral and extremely alkaline, respectively. Soil pH naturally becomes lower over time due to many reasons. The three principal reasons that may cause a decrease of soil pH are due to leaching of calcium from the soil by acid rain, application of ammonium-based fertiliser and decay of the organic matter in the soil.



Nitrogen oxides (NO_x) and sulphur dioxide (SO₂) released into the atmosphere from the burning of fossil fuels and also resulting from natural sources like volcanoes react with moisture, oxygen and other elements to produce nitric and sulfuric acids which then mix with precipitation and fall to the ground as acid rain [9]. The acid rain then leaches out calcium from the soil, dropping pH, and consequently the acidity of the soil increases due to the addition of hydrogen to the soil. Similarly, the application of ammonium-based fertiliser increases the acidity of the soil by converting ammonium nitrogen to nitrate and hydrogen ions. The free nitrate that is not taken up and absorbed by plants then seeps out from the root zone, leaving hydrogen ions behind, with the acidity of the soil increasing. Likewise, the decay of organic matter also increases the acidity of the soil.

Calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) are the main cementitious compounds that provide bonding during stabilisation with calcium-based stabiliser (cement or lime). However, sulphate ions in the soil are capable of reacting with cementitious compounds, causing a chemical failure mechanism in stabilised soil. The reactions between C-S-H or C-A-H with sulphate ions will then produce calcium sulfoaluminate hydrate (ettringite) destroying the adhesion holding the materials together [10,11]. Therefore, in preventing the formation of ettringite in the stabilised soil, investigating the geochemical properties of soil is a prerequisite before deciding whether to use cement, lime or other stabilisers that are inert to sulphate ions. Accordingly, this paper aims to investigate the geochemical properties of marine clay samples collected from Batu Pahat, Johor, Malaysia.

2. Material and methods

The marine clay samples were collected from Universiti Tun Hussein Onn Malaysia (UTHM) after removing about 1.5 m of topsoil. The UTHM campus is located at Parit Raja town in Batu Pahat District, Johor, Malaysia. The sampling area displays a moderately flat terrain with ample watercourses. The area also displays a surface in a dampened condition with petite infiltration ability of about 11.3 mm/hour [12].

The physical properties, pH and loss on ignition (LOI) of the marine clay were tested based on the British Standard procedures [13,14]. The chloride ions in the marine clay were tested as per the procedure according to the American Society for Testing and Materials (ASTM) [15]. While the concentration of sulphate, carbonate and nitrate ions in the marine clay was tested using the standard procedure issued by the American Public Health Association (APHA) [16–18].

3. Results and Discussion

The results of the geochemical and physical properties of the marine clay are presented and discussed in this section

3.1. Physical properties of the marine clay

The results of the natural moisture content, liquid limit, plastic limit, optimum moisture content (OMC) and maximum dry density (MDD) were 67%, 65%, 26 %, 25% and 1440 kg/m³, respectively. The marine clay was classified as clay of high plasticity (CH). Figure 1 displays the result of the particle size distribution of the marine clay.

From the results of testing the physical properties of the marine clay, the soil was found to have poor physical properties due to LL of 65 % (higher than 35%), PI of 39% (higher than LL-30) and an abundance of fine particles smaller than 65 µm, constituting more than 98% of the entire sample as shown in Figure 1. The sample contained only 0.08% of particles larger than 2 mm and about 1.24%, 58.12% and 40.56% of soil particles between 2 mm and 63 µm, 63 µm and 1µm and below 1 µm, respectively. Consequently, the marine clay was considered an unsuitable material for use as subgrade material as per [19] specification. The marine clay was also classified as clay of high plasticity (CH) making it unsuitable for use as foundation material unless treated.

The physical characteristics of the marine clay based on the above results, confirmed that marine clay is not suitable for use for construction purposes. Therefore, a suitable stabiliser for improving the properties of the soil is needed

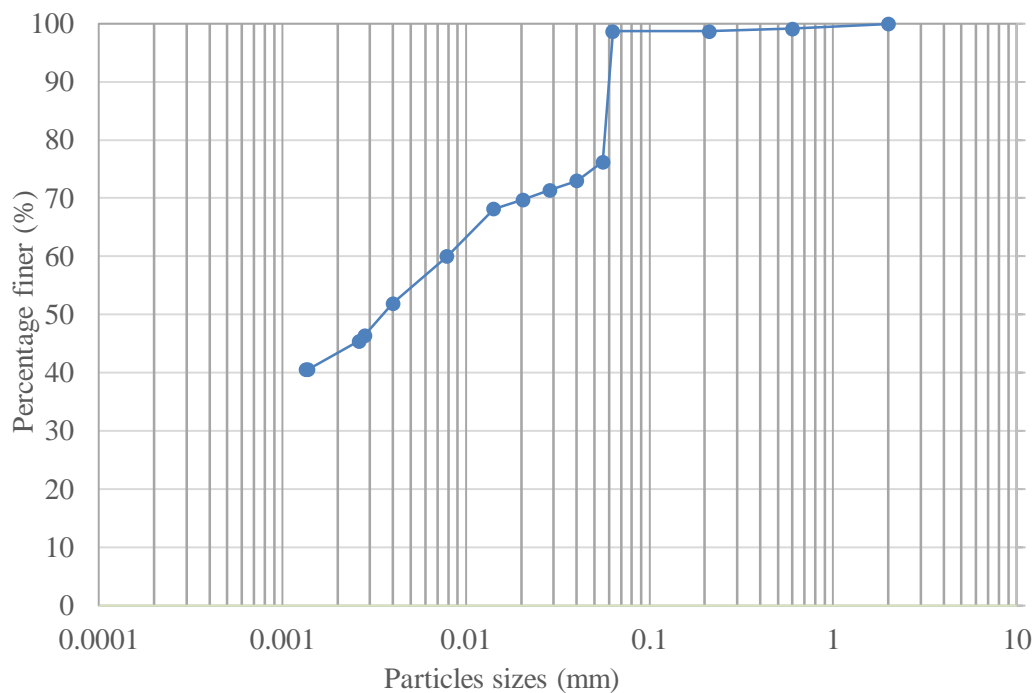


Figure 1: Particle size distribution chart of the marine clay

3.2. Geochemistry

The geochemistry of the soil was next tested by measuring six parameters: pH, LOI, chloride, sulphate, carbonate and nitrate contents. Table 1 shows the results and the corresponding standard procedures applied in performing the tests.

Table 1: Geochemistry of the marine clay

Parameters	Unit	Results	Method of testing
pH	-	3.25	[14]
Loss on ignition, LOI	%	8	[14]
Chloride as Cl ⁻	mg/l	287	[15]
Sulphate as SO ₄ ²⁻	mg/l	6071	[16]
Carbonate as CO ₃ ²⁻	mg/l	< 1	[17]
Nitrate as NO ₃ ⁻	mg/l	22	[18]

From the results of the geochemistry tests of the marine clay shown in Table 1, the concentrations of sulphate, chloride and nitrate ions in the soil sample were shown to be 6071 mg/l, 287 mg/l and 22 mg/l that represent about 95%, 5% and 0% for the sulphate, chloride and nitrate ions, respectively as demonstrated using the pie chart in Figure 2. It can be seen that the sulphate ion in the soil is the primary cause of acidity of the marine clay. Therefore, the primary concern in the improvement of the said marine clay is the sulphate ion.

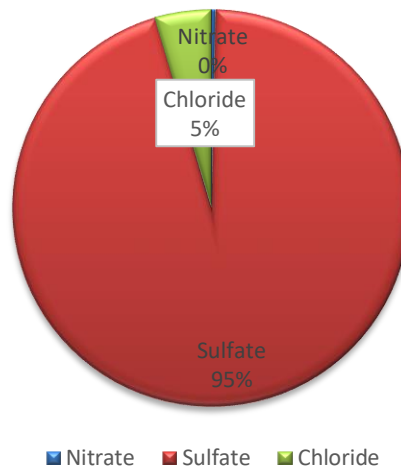
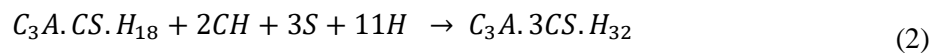
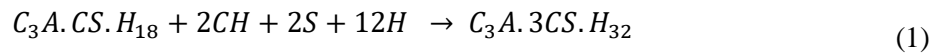


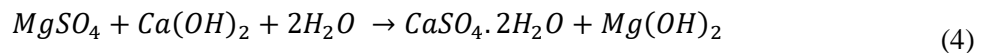
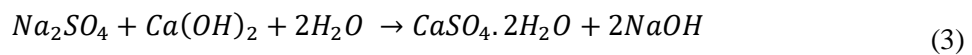
Figure 2: Distribution of concentration of sulphate, nitrate and chloride ions in the marine clay.

As mentioned previously, sulphate ions cause a chemical failure mechanism in soil stabilised with cementitious compounds. The sulphate ions from alkali earth sulphate (calcium sulphate or magnesium sulphate) and alkali sulphate (sodium sulphate or potassium sulphate) react with the calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) producing ettringite as the sulphate dries up [10]. Equations [1-4] show the chemical reactions for the formation of the ettringite.

Sulphate ion + Calcium aluminate hydrate and Calcium hydroxide + water → Calcium sulphotoaluminate hydrate (Ettringite).



Sulphate ion + Calcium aluminate hydrate and calcium hydroxide + water → Calcium sulphate hydrate (gypsum).



The sulphate ion concentration in marine clay is the determining factor that dictates how the calcium base stabiliser will be affected in the stabilised soil. The existence of sulphate as little as 300 mg/l may trigger the formation of ettringite that can induce swelling disorder in the stabilised soil [20]. Cameron [20] classified the risk of sulphate attack as shown in Table 2.

From the results of the sulphate contents of the marine clay sampled, the sulphate concentration was 6,071 mg/l showing there is moderate to the high-risk tendency of forming ettringite if the marine clay is stabilised with lime or cement. Furthermore, there is also a high likelihood of the sulphate attacking the concrete of the foundation of any infrastructures founded on this marine clay.

The geochemistry results of the marine clay also showed that there was about 287 mg/l of chloride ions that contributed to about 5% of the total acidity of the sample. Contradictory to the sulphate ions, the chloride ions favour the formation of a better pozzolanic compound leading to the formation of a cementation compound of calcium aluminate hydrate (CAH) and calcium silicate hydrate (CSH) [8]. Therefore, the chloride ions in the marine clay will have a positive effect on the stabilised soil if cement or lime is used as the stabiliser.

Table 2: Effect of sulphate concentration on the soil for stabilisation (sources: [11,20]).

Concentration of Sulphate (mg/l)	Remarks
300 to 500	Can induce swelling disorders favourable for the formation of ettringite.
< 3,000	Minor distress and low probable destructive reaction (minimal to be concerned about).
3,000 to 5,000	Reasonable distress typically does not result in a destructive disorder, however, may cause local distress (moderate risk).
5,000 to 8,000	Moderate to high risk.
> 8000	High risk to stabilise with lime.
>10,000	Unsuitable for lime stabilisation due to the high risk of sulphate-made disorder and failure.

The concentrations of nitrate ions in the marine clay as tabulated in Table 1 is only 22 mg/l. The nitrate ions have moderate detrimental effects on the soil stabilised with cementitious compounds through an acidic-basic reaction if the concentration of nitrate compounds is sufficient [21]. At least 8000 mg/l of ammonium nitrate in the soil can accelerate the setting time of stabilisation. Similarly, sodium or potassium nitrate can also cause expansion of the soil stabilised with cementitious compounds [21]. Nevertheless, considering the concentration nitrate ion in the marine clay under review is only 22 mg/l, so, is too small and not likely to cause any effect.

In contrast, the carbonate ion is an organic matter stabilisation agent that favour the mechanisms chemical stabilisation and can neutralise the soil pH [22]. However, the concentration of the carbonate ion in this marine clay is only less than 1 mg/l. Therefore the effect of carbonate ion is also negligible that is why the soil has the acidic pH because the concentration of the carbonate in the soil too small to neutralise the soil acidity. Furthermore, the result concerning the loss on ignition showed that the sample contained 8% of organic matter which will decay in the soil, contributing to the acidity of the sample.

4. Conclusions

Several laboratory experiments were performed on marine clay samples collected from Batu Pahat, Johor. The following conclusions are drawn from the findings of the study, characterising the geochemical characteristics of the marine clay:

1. The marine clay has poor physical properties that need improvement before used for construction purposes.
2. The marine clay has a pH of 3.25 and containing 8% organic matter. The sample also contains 6071 mg/l, 287 mg/l, and 22 mg/l of sulphate, chloride and nitrate ions respectively. The carbonate content in the sample is less than 1 mg /l.
3. The sulphate and chloride ions in the marine clay sample contributed to 95 % and 5 %, respectively of the acidity of the soil while nitrate and carbonate ions in the sample were of a negligible percentage.
4. There is a risk towards triggering the formation of ettringite and consequential decomposition of the stabilised soil if the marine clay is stabilised with any calcium base stabiliser like lime or cement. Thus, the marine clay is not suitable for stabilising with lime or cement. Moreover, particular attention should be taken during the design of any infrastructure foundations in the study area due to the high tendency of sulphate attack on the concrete of the foundation.

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