Observation of pH Value in Electrokinetic Remediation using various electrolyte (MgSO$_4$, KH$_2$PO$_4$ and Na(NO$_3$)) for Barren Acidic Soil at Ayer Hitam, Johor, Malaysia

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Abstract. Barren acidic soil collected at Ayer Hitam, Johor Malaysia was recorded at pH value of 2.36 with relative humidity of 86%. This pH value is not suitable for the growth of any plants especially for the soil stabilization purposes. Gradation weathering within the range of 4 to 6 indicates an incomplete/partial weathering process. The soil grade in this range is known as a black shale mudstone. Beside, this also influences to a factor of the high surface water run-off at this particular soil species. As the acidic pH become a major problem for soil fertilizing hence an appropriate technique was implemented known as ‘Electrokinetic Remediation’, EKR. This technique has a great potential in changing the soil pH value from acidic to less acidic and also kept maintain the pH at the saturated rate of electrochemical process. This research study presents the monitoring data of pH value due to the effect of various electrolyte consist of 0.5M of MgSO$_4$, KH$_2$PO$_4$, and Na(NO$_3$). Here, the distilled water (DW) was used as reference solution. The electric field was provided by dipping two pieces of identical rectangular aluminum foil as anode and cathode. The EKR was conducted under a constant voltage gradient of 50 V/m across the sample bulk at 0.14 m length measured between both electrodes. The data collection was conducted during the total period of 7 days surveillance. The variation of pH values at the remediation area between anode and cathode for various type of electrolyte indicates that there are a significant saturated value as it reaches 7 days of treatment. During the analysis, it is found that the highest pH value at the remediation area after 7 days treatment using Na(NO$_3$), KH$_2$PO$_4$ and MgSO$_4$ was 3.93, 3.33 and 3.39 respectively. Hence from the last stage of pH value observation, it can be conclude that the best electrolyte for barren soil treatment is Na(NO$_3$) whereby it contribute to highest pH value and turn the soil to be less acidic.

Keywords: Soft soil, geo-disasters, geo-remediation.
1. Introduction
Barren acidic soil is one of the major causing for surface erosion. This particular soil can be classified as sedimentary soil with weathering grade range of 4 to 6. The soil grade in this range is known as a black shale mudstone. This sedimentary soil become acidic after acidification process [1]. Acidification of soil is a complex process (changes) occur in soil properties such as decrease in pH value, release of base cations from the sorption complex involving rainfall and leaching, acidic parent rock material, organic decay and high yielding crops [2]–[4]. This process forming infertile and unfavorable soil [5]. The process of soil acidification took place when the subsoil or parent material containing acidic ion are exposed to the atmosphere.

Term “barrens” is used to describe regions that have poor nutrient to support vegetative species. Most vegetation species was adapted to their ecology. Barren soil can be express as poor farmland, or lacks in aesthetic landscape while the ecologist describes barren soil as edaphic drought and soil infertile [6]. Most barren soils contained pyrite mineral and the oxidation of pyrite resulting the formation of iron hydroxide minerals, sulfate and sulphuric acid. Chemical reaction of oxidation of pyrite minerals:

\[ FeS_2 + 3 \frac{1}{2} O_2 + H_2O \rightarrow Fe_2SO_4 + 2 H^+ + SO_4^{2-} \]  
(1)

\[ H_2SO_4 \leftrightarrow 2H^+ + SO_4^{2-} \]  
(2)

From the Eq. 1, FeS$_2$ is the empirical formula for pyrite. The presence of excess oxygen and water produce a product of FeSO$_4$, which are ferrous sulphate and 2H$^+$ + SO$_4^{2-}$ stand for dissociated sulphuric acid shown in Eq. 2. When this dissociated sulfuric acid rendering to the water catchment area, it will cause acidification process. These related reactions are accountable for producing an enormous amount of acidity thus reducing the presence of sulphur in the soil [7], [8]. Oxygen level increase by drainage or excavation of the ground surface. From Eq. 1 and Eq. 2, the formation of hydrogen ion has increased the availability to react with other acid functional group that then will be dissociated. Eq. 1 and Eq. 2 shows barren soil is an acidic soil where the chemical percretion during weathering produce sulphuric acid after oxidation process and this acidic behavior eliminate the nutrients in soil for vegetation growth.

Electrokinetic remediation, EKR is a promising technology for the elimination of contaminated fine-grained soils has been studied broadly since the 1980s [9]–[11]. The low-level direct current, DC in the range of mA/cm$^2$ applies to soils within a particular treatment time. This effect will influence to a change of fundamental soil physic-chemical and hydrologic properties by chemical or non-chemical used. These chemical acts as an electrolyte that change the effect of the chemical speciation and transport of soil constituents, including metals [10], [12]. The electromigration takes places simultaneously with the electroosmosis. Here, the ions species at the anode are replaced by chemical electrolyte according to the cation exchange capacity, CEC. During this process, the bigger cations replacing smaller cations at the same valance and higher valance replacing smaller valance. This process occurs instantaneously with the migration of negatively charge ions to the anode and positively charge ions to the cathode [13], [14].

As the barren soil becomes a major problem causing soil infertility for stabilization purposes, therefore, the aim of this study is focus to the effect of pH change using various type of electrolyte for EKR treatment.
2. Material and Method

1.1. Soil Specimen Preparation

The soil specimens were prepared with a consistent method through all experiments. 1.5 time liquid limit, LL of deionized distilled water, DW was used to form slurry soil specimen by mixing with the barren acidic clay soils with deionized water to achieve 90% moisture content to produce a homogeneous sample. Approximatively, 4 kg of DW was used to mix with 20 kg of barren acidic soil by gradually added to ensure consistency of mixing. These slurry samples mixed using Kenwood mechanical mixer and blended thoroughly for 30 minutes with medium speed. Two mixtures of slurry samples needed to fill up the ¾ height of the tank with the total amount of 10 kg and 10 kg respectively achieving 40 % of moisture content for all test samples.

The initial height of the slurry is 236 mm for all tests samples before approximately 1 kPa of the surcharge was added for 24 hours to avoid soil particle migration or spill off via the drainage. Another 16 kPa of the surcharge was added to consolidate the slurry sample until reached final height of 180 mm. After pre-consolidation, the thin solid plastic walls were removed at both ends of the main compartment and replaced with aluminum electrodes. The soil samples were reconsolidated under the same loading as the last consolidation (17 kPa) for about 24 hours before released upon EKR testing. Subsequently, the electric current were turned and monitored throughout the test durations to make sure a good contact between soils and electrodes. Physical and chemical properties of the treated soil were carried out along the soil profiles that were divided into two sections from the anode to the cathode.

1.2. Basic properties of the Soil Sample

The physic-chemical properties of Ayer Hitam barren acidic soil was investigated using laboratory testing accordance with British Standard, BS 1377:1990 as shown in Table 2. The Ayer Hitam barren acidic soil was categories as clayey SILT with the percentage of silt higher than clay approximately 50.33 % and 49.67 %. The liquid limit, LL for Ayer Hitam barren acidic soil is 26.66 during the plastic limit, PL was 10.48 which give the plastic index, PI of 19.25. Average specific gravity identified was 2.53 with an initial pH value of 2.36 and electrical conductivity, EC of 2.86.

Table 1. Properties of Barren Acidic Soil.

| Parameter                     | Value |
|-------------------------------|-------|
| **Particle Size Distribution:** |       |
| Silt                          | 50.33 |
| Clay                          | 49.67 |
| **Atterberg Limit:**          |       |
| Liquid Limit                  | 26.66 |
| Plastic Limit                 | 17.95 |
| **Average Specific Gravity (G_s)** | 2.53 |
| **Initial pH Value**          | 2.36  |
| **Electrical Conductivity**   | 2.86  |

1.3. Development of Experimental Apparatus

These remedial systems were set up in laboratory model using acrylic PVC-U to avoid current leaching. The EKR model shown in Figure 1 consists of the anode compartment, soil specimen compartment and cathode compartment with an overall dimension of 460 x 340 x 300 mm. The dimension of the soil specimen compartment (main compartment) is 180 x 320 x 300 mm and the other two small compartments is 100 x 320 x 300 mm. The thickness of the EKR model is 10 mm
sealed with heavy duty silicon to prevent electrolyte leaking. Aluminium electrode used was with the dimension of 320 x 300 mm and polished both sites to minimize the expose of oxygen.

**Table 2.** The EKR Experimental Condition.

| Exp. No. | Anolyte   | Catholyte | Temperature, ºC and Humidity, % |
|----------|-----------|-----------|---------------------------------|
| 1        | DW        | DW        | 30, ≈80 %                       |
| 2        | 0.5 M MgSO₄ | DW        | 30, ≈78 %                       |
| 3        | 0.5 M KH₂PO₄ | DW        | 32, ≈68 %                       |
| 4        | 0.5 M Na(NO₃) | DW        | 28, ≈86 %                       |

Direct current, DC power supply used was from model GW INSTEK with a constant voltage gradient of 50 V/m for 7 days treatment with assessed of pH value and electric current every 24 hours. The pH value measured using Mettler Toledo Perfect Seven Pro and calibrate with the solution-temperature gradient graph.

**Figure 1.** Schematic Drawing of EKR Testing Model [15].

### 3. Result and Discussions

Figure 2 shows monitoring data of pH value from different EKR system for 7 days. Overall observation shows at the beginning of the test indicate that the pH value recorded was fluctuated and slightly constant after days 3 onwards. Remediation of acidic soil using pure system shows an increasing of pH value from day 1 to days 4 with value of 2.36, 2.55, 2.67 and 2.99 and decreasing from days 5 to day 6 with value of 2.85 and 2.72 before increase to 2.88 at days 7. The graph pattern shows that the after the introduction of electric field by EK remediation using DW as an anolyte and catholyte increase the pH value of the soil sample from day 1 to days 4 and slightly constant pattern at days 5 to days 7 because of the adaption of electric field onto the soil sample.

The pH value of sample treated with 0.5 M of MgSO₄ as an anolyte and DW as catholyte shows decrement from day 1 to days 7 from 5.09, 4.57, 3.93, 3.67, 3.59, 3.42 and 3.39. The immediate change of pH value from 2.36 at the soil sample to 5.09 was due to influence of electric field by EKR
and higher pH value of 0.5 M of MgSO₄ than soil sample. After day 1, the graph shows decreasing of pH value since the anolyte used altered the concentration of acidic soil sample. It is also can be conclude that the 0.5 M of MgSO₄ promote the addition of sulphate to the soil sample.

Figure 2. pH Value of EKR System with Days

The pH value at the 0.5 M of KH₂PO₄ shows increment from day 1 to days 5 with value of 2.36, 2.87, 3.55, 3.66, and 3.79 before decreased at days 6 and days 7 with value of 3.55 and 3.33. The increasing of pH value of soil sample was due to introduction of alkaline electrolyte with the presence of electric field that migrate the electrolyte through the soil sample area. The similar pattern of pH value also can be observe by using 0.5 M of Na(NO₃) which shows immediate increase on days 2 with value of 6.78 and drastically decrease at days 3 with value of 4.15 before maintaining at days 4 to days 7 with value of 3.90, 3.92, 3.93 and 3.93. based on the results, the optimum state of 0.5 M of KH₂PO₄ is at days 5 with value of 3.79 and the optimm state for 0.5 M of Na(NO₃) is on days 2 with value of 6.78.

The inconsistency of this pH result might be due to the electrolysis process. This statement complies with Park et al., [6] which mention during electrolysis reaction, the H⁺ ions moves towards the cathode regions, and OH⁻ ions move towards anode regions. Electromigration was affecting the pH value, electric current and voltage gradient. The ionic mobility of H⁺ ions is 1.78 times faster than the OH⁻ ions. The OH⁻ ions produced were neutralized by the catholyte. Giannis et al., [16] states that the acidic soil pH indicates that some of the H⁺ ions produced at the anode by electrolysis migrated into the soil column. The OH⁻ ions produced was neutralize using catholyte.

Another factor that considered as mechanisms that affecting the variation of pH value is the soil-electrode contact. This factor varied upon insertion of the electrode during sample preparation. These electrode-soil contact interfaces were essential after pre-consolidation and post-consolidation after the exchange of thin-wall solid plastics wall with the electrode. These exchanging produces a gap between electrode and soil thus manipulated the volume of the direct current electric field across the soil sample. The post-consolidation should be carry out at least 24 hours or more with the same pressure of surcharge to minimize the gap between electrode-soil contacts.
4. Conclusion
From this observation, the summarize of the finding are as follows;

i. Electric field from the EKR influencing the changes of pH values by transport the ions across the soil sample. This electro-migration activities replacing the anions and cations according to its exchange capacity where influencing the deposition of H+ and OH- ions across the soil sample.

ii. The most suitable anolyte as a catalyst to increase the pH value of this barren acidic soil is 0.5 M of Na(NO3). This anolyte act as buffer providing baseline, supply nutrients and facilitates the pH value control thus it agree with the past research done by Li et al., [9].

iii. The result presented for the other anolytes agree with the finding from past research done by Park et al., [6] and Giannis et al., [17] The results from observing data showed that there are several important mechanisms relating to the electrochemical effects. The pH value profiles were influenced by the ionic concentration of the fluid within the soil samples. Style and spacing

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