EFFECT OF SELECTED FACTORS ON THE CURRENT FLOW AND VOLTAGE LOSS AT ELECTRODES DURING ELECTROCHEMICAL TREATMENT OF A LATERITE

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ABSTRACT

In this paper, laboratory scale study was conducted to investigate the current flow and voltage loss at the electrodes in the electrochemical treatment of a tropical laterite. Three different tests using calcium chloride (CC) as anolyte and sodium chloride (SC) as catholyte (NC); SC as anolyte and Phosphoric acid (PA) as catholyte (NP) and CC as anolyte and PA as catholyte (CP) were conducted at two different voltage gradients of 1 and 2 V/cm. Perforated Titanium sheet were used as the electrodes. Current flow and voltage at the electrodes were measured using standard methods. Effects of selected factors on the current flow and voltage losses were monitored. Energy consumption analysis was provided. The study revealed that the highest currents were consistently generated in CP tests while the lowest current was generated in NC tests. The highest voltage losses of about 75% were recorded in 40NC and 40CP tests, although, the conductivity of CC and SC kept increasing during the test. It was revealed that the applied voltage and the type of electrolyte were significant factors affecting the current generated in the system at 95% confidence level. Electrolyte used was found to be a significant factor affecting the voltage loss at the electrodes at 95% confident level. Energy analysis revealed that CP was not economical. It was concluded that the PA was a better electrolyte that could sustain current generation and minimize voltage loss at the electrodes.

Keywords: Electrochemical Treatment, Soil Improvement, Anolyte, Catholyte, Voltage Drop

INTRODUCTION

Increasing urbanization has led to the construction of structures on sub optimal soil. The injection of chemical ions into in situ soil using Direct Current (DC) voltage is a promising technology (Alshawabkeh and Sheahan, 2002) for stabilising sub optimal soil. This process of stabilisation usually referred to as electrochemical stabilization (ECS) or electrogrouting (EG) is suitable for low permeability foundation soil and where mixing and placing with suitable stabilizing agents is not possible. ECS involves the application of DC voltage across a moist soil through two electrodes which are usually put in solution (electrolyte) containing the stabilizing ions to be injected.

The injection of ions into the soil can be achieved through one or both of electro-osmosis (EO) and electro-migration (EM). EO and EM are geochemical reactions that occur due to the applied DC voltage. EO is the movement of pore fluid from one electrode to the other (usually from the anode to the cathode). EO can thus lead to reduction in the water content of treated soil leading to increased shear strength. EM is the movement of chemical ions to oppositely charged electrodes. EM results in transporting ions into the soil, these ions can in turn react together and form insoluble cementitious compounds within the soil.

The distribution and intensity of the electric field generated during electrochemical treatment is a key parameter to the efficiency of the process (Lo *et al.*, 1991; Reddy and Karri, 2006; Rittirong *et al.*, 2007). Rittirong *et al.* (2007) showed that the formation of cementing constituents is directly proportional to the intensity of the applied electric field. It was shown by Lo *et al.* (1991) that the electric curent is a governing parameter for the process to occur, no matter the amount of the applied voltage. This relationship can be expressed as follows (Reddy and Cameselle, 2000):

$$v_{eo} = \frac{D\ae}{\varsigma\hat{e}}i \qquad (1)$$

where:

v_{eo} is electro-osmotic velocity (m/V-s); D is dielectric constant; ς is zeta potential (V); i is

applied current (A); η is viscosity of the pore fluid and $\varkappa$ is electrical conductivity (S/cm).

$$v_{em} \quad u_i z_i \hat{o} nFE \qquad (2)$$

where:

v_{em} is electromigrative velocity (m/s); u_i is ionic mobility of ion i (m^2/V-s), z_i is charge of ion i, τ = tortuosity; n is porosity; F = Faraday's constant (96,487 C/mol electrons) and E is electric field strenght (V/m).

The equations above show that the velocities of EO amd EM are a function of the electric current.

It has been shown that the electric current gradient responsible for the EO flow or EM of ions is not the total applied voltage gradient, but rather the gradient effectively transmitted to the soil (Lefebvre and Burnotte, 2002). Lefebvre and Burnotte (2002) stated that only a small portion of the electrical potential applied at the electrodes is effectively transferred to the soil mass due to large potential losses at the soil-electrode contact. This implies that in addition to the electric current, voltage drop at the electrodes are important parameters affecting the effectiveness of the treatment process (Mohamedelhassan and Shang, 2001; Reddy and Karri, 2006; Rittirong et al., 2007).

Previous studies have revealed that elcetrochemical treatment is effective in improving the geotechnical properties of soft soil and /or laterite, but literature on effect of electrolytes on the treatment process is rare. This indicates that there is the need to document effect of electrolytes on the treatmet process. This study was, therefore, carried out to determine the effects of some electrolytes that are commonly used during ECT on the current and voltage losses at the electrodes during the ECT of a laterite.

MATERIALS AND METHODS

A laterite (with Silicon oxide, SiO_2 to Aluminium oxide, Al_2O_3 ratio of 0.6) was prepared to a bulk density of 1.63 g/cm^3 at a moisture content of 50% to represent a soft soil. The soil sample was subjected to electrochemical treatment in a laboratory set up as shown in Figures 1 and 2. A DC voltage of 20V and 40V were applied through perforated Titanium sheet electrodes inserted in either 1M calcium chloride (CC) or 0.01M sodium chloride (SC) as the anolyte. Either 1M phosphoric acid (PA) or SC was used as the catholyte. The experimental program is presented in Table 1.

During testing, the current flow in the system and voltages between three voltage probes for some experiments (20TT, 20NN, 20NP, 40NC, and 40NP) and six voltage probes for others (20CP, 40CP, 40NCr, 40NPr and 40CPr) along the length of the soil sample were measured using a multimeter at regular time intervals of 12 hours. Voltages at different point along the length of the soil were measured (with reference to the cathode. The conductivity of the electrolytes was measured with time as treatment progressed. The polarity of the setup was reversed in some tests (40NPr, 40NCr and 40CPr).

Initial tests were carried out on soil mixed with 0.01M NaCl, while tap water was used as electrolytes (20TT) and soil mixed with distilled water, while 0.01M NaCl was used as electrolytes (20NN) in order to test the effect of soil conductivity on the current and voltage at the electrodes. The voltages between the cathode and the first probe (VI) are represented as 20NN_CV1 and 20TT_CV1 for 20NN and 20TT, respectively. The voltages between the anode and the last probe (V3) are represented as 20NN_AV3 and 20TT_AV3 for 20NN and 20TT, respectively. The voltages effectively transferred into the soil (between the first and last probes in the soil) are also represented as 20NN_V3V1 and 20TT_V3V1 for 20NN and 20TT, respectively.

The results obtained were analyzed using either one way ANOVA or T tests to ascertain the significance of the effect of applied voltage, polarity reversal and the electrolytes on the current generated and the voltage drops at the electrodes.
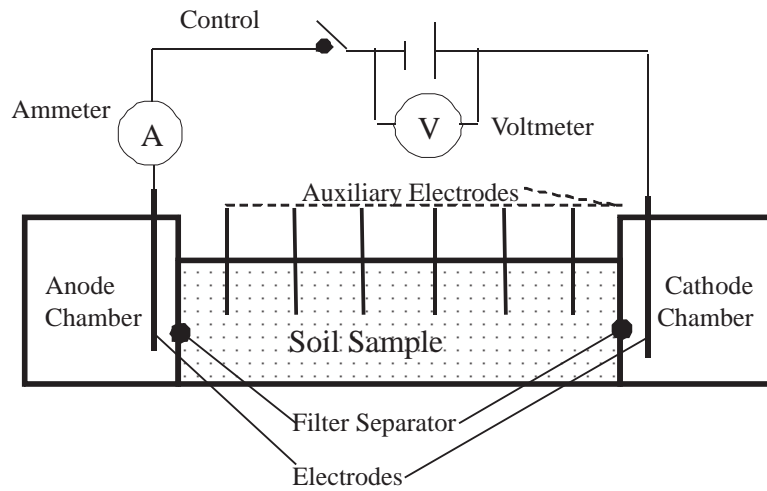
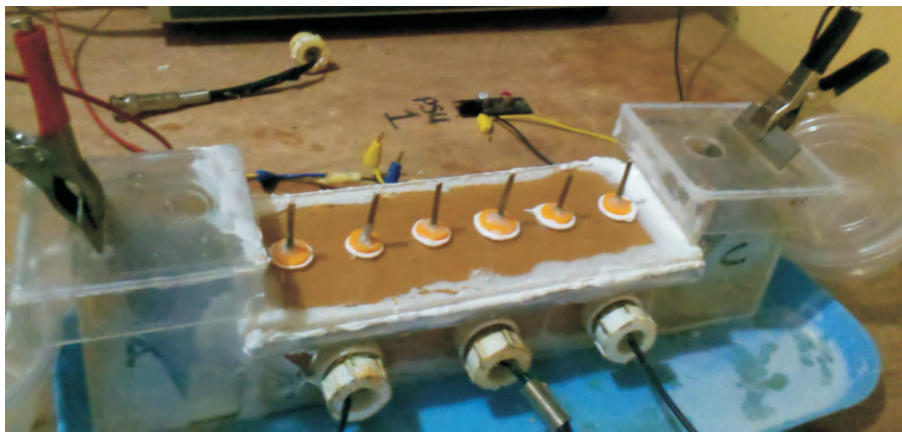Figure 1: Schematic of Laboratory Set up

Figure 2: Laboratory Set up of the Treatment Process

Table 1: Experimental Program for the Study

S/N	Tests	Catholyte	Anolyte	Voltage gradient
1	20NP	1M H_3PO_4	1M NaCl	1 V/cm
2	20CP	1M H_3PO_4	1M $CaCl_2$	„
3	40NP; 40NPr	1M H_3PO_4	1M NaCl	2 V/cm
4	40NC; 40NCr	1M NaCl	1M $CaCl_2$	„
5	40CP; 40CPr	1M H_3PO_4	1M $CaCl_2$	„

RESULTS AND DISCUSSION
Effect of Soil Conductivity on the Current and Voltage Loss at the Electrode in Tests 20NN and 20TT

The electric current in tests 20NN and 20TT is presented in Figures 3. The figure reveals that the current in both tests followed same pattern until about after 60 hours of treatment when the current in test 20NN started dropping and that in test 20TT kept increasing. The increasing current in 20TT is probably due to higher conductivity of the soil due to the NaCl directly mixed with the soil.

The voltages measured during treatment are presented in Figure 4. The voltage loss at the electrodes at the beginning of the experiment was more in test 20TT as shown in Figure 4. As the experiment proceeded, the voltage losses fluctuated but the highest voltage loss was still recorded at the anode of test 20TT as shown in Figure 4. The voltage (V3V1) that was effectively transferred into the soil was more in test 20NN than in 20TT as presented in Figure 4. From the figure, the voltage (V3V1) reduced as the experiment proceeded in test 20NN but increased in test 20TT with the same value recorded at about 100hrs of treatment.

Comparing the voltage loss at the cathode of both experiment 20TT and 20NN, more loss was recorded in experiment 20NN. The voltage loss followed similar pattern with that in 20TT higher than that in 20NN but after about 70 hours of the experiment, the loss in experiment 20NN increased while that in experiment 20TT decreased as shown in Figure 4. The reduction in the voltage loss at the cathode led to increase in the current flow in the system for test 20TT. The voltage loss at the anode for both tests also followed similar pattern at the beginning of the experiment with that in 20NN lower than that in 20TT but after about 60 hours of the experiment, the voltage loss at the anode for 20NN continued to reduce while that in test 20TT continued to increase. These results revealed that improvement in contact at the electrode was more effective for test NN with reduction of power loss at the anode which is usually the main point of voltage loss. This observation is similar to that of Lefebvre and Burnotte (2002) in which the mail point of power loss was at the anode. Soil samples used for subsequent tests were therefore not mixed with NaCl but distilled water. This decision was also based on the feasibility of mixing NaCl with soil insitu. The power consumption in both tests 20NN (0.0146W) and 20TT (0.0142W) was also comparable.
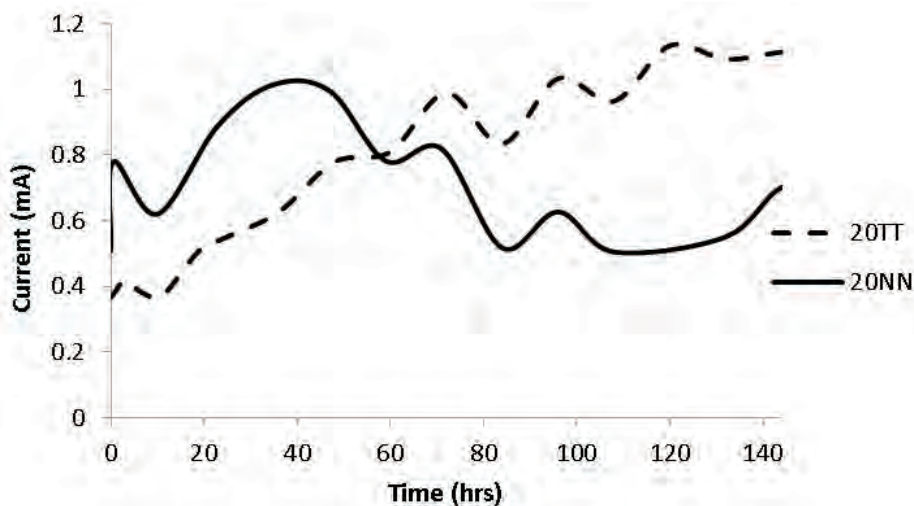

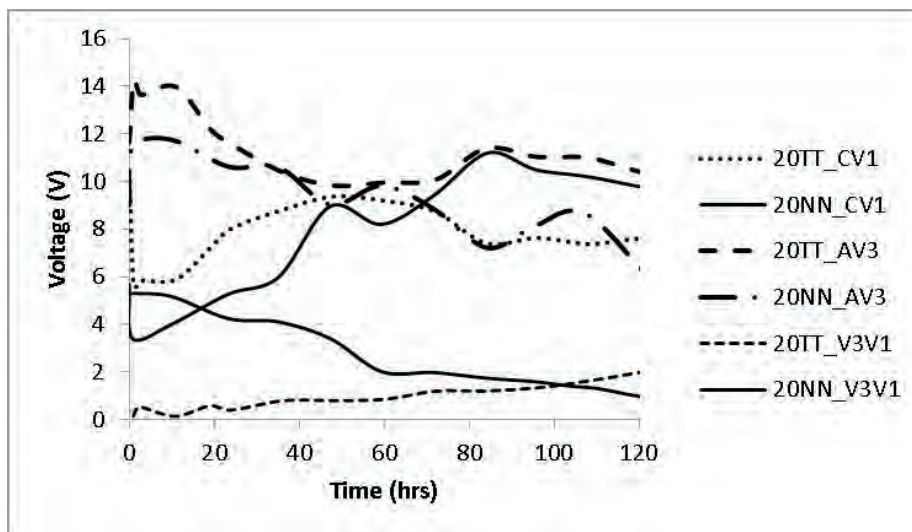Figure 3: Flow of Current with Respect to Time

Figure 4: Voltages across the Electrolyte

Current and Potential Gradient in Different Tests

The current and potential gradients at both electrodes are presented in Figures 5 to 12. The current generated in tests containing PA as catholyte (NP and CP tests) generally fluctuated with time till the end of the experiments. Current generated in CP were consistently higher than that generated in either NP or NC. The current in test 40CP was very high starting at 16.197 mA, fluctuated a bit and increased to a maximum of 30.1 mA at the end of the experiment as shown on the secondary axis in Figure 9.

The current in tests NC increased to a peak before reducing. This behaviour agrees with most of those reported in the literature, although, precipitation of ions has been the reason given for this behaviour (Pamucku *et al.*, 2004; Reddy and Karri, 2006). Another reason for this behaviour is voltage drop at the cathode which kept increasing from the beginning of tests till the end as presented in Figure 7.

Although the voltage drop at the cathode for NP tests also increased, the increment was not as much as in NC tests. The initial voltage drop at the beginning of tests 40NC and 40CP were 11V and 4V, respectively. These values increased to almost 30V at the end of the experiment. The initial voltage in test 40NP was 2.46V and increased to only about 6V at the end of the experiment. This was probably so because of higher conductivity of PA than NaCl used as the catholyte. These results showed that the electrolyte affected the current in the treatment considerably.

The effect of the electrolyte on the current was further shown as the current and voltage drop at the cathode fluctuated each time the polarity of the set-up was reversed as presented in Figures 10 to 12. The voltage drop was usually more whenever NaCl or $CaCl_2$ was the new cathode.

The behaviour of current generated in NP tests was however, contrary to those reported in the literature (Alshawabkeh and Sheahan, 2002) where there was a constant increase then decrease in the current. The current in tests containing both CC and PA was the highest (when compared with both NC and NP tests) starting at 16.197 mA, fluctuated a bit and increased to a maximum of 30.1 mA at the end of the experiment as shown in Figure 7.

Statistical analyses of the results using T test revealed that the applied voltage is a significant factor (at 95% confidence level) affecting the current generation within the system as shown in Table 2 for systems treated with same electrolytes but different voltages. Polarity reversal also had significant effect on test NC and NP with p value less than 0.05 in both cases. There was no significant effect of polarity reversal however, in tests CP as p value was more than 0.05, but it was significant at 90% confidence level. The type of electrolyte used was shown to have significant effect on the current generation during treatment as shown in Table 3 with p consistently less than 0.05 for all treatment types.
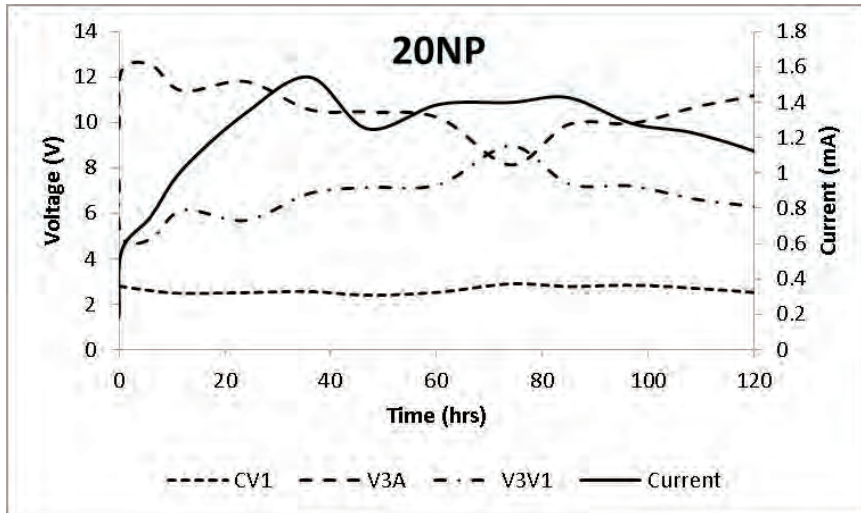
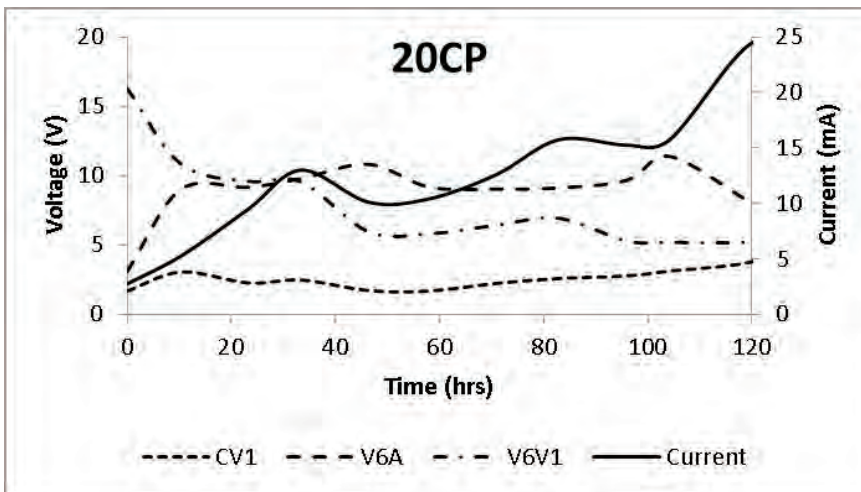Figure 5: Current Flow and Voltage across the Electrolyte (20NP)

Figure 6: Current Flow and Voltage across the Electrolyte (20CP)
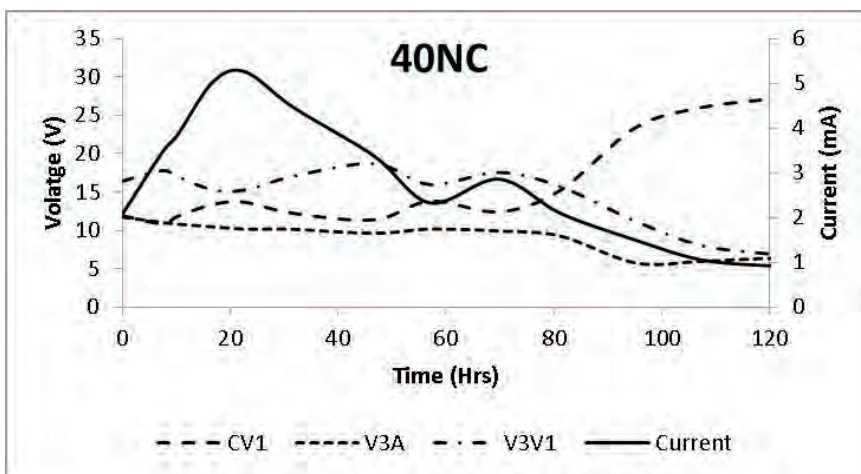

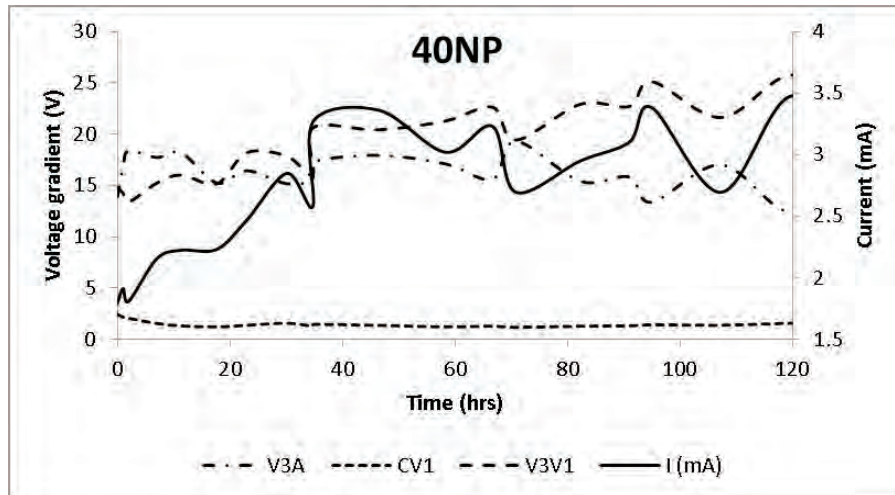Figure 7: Current Flow and Voltage across the Electrolyte (40NC)

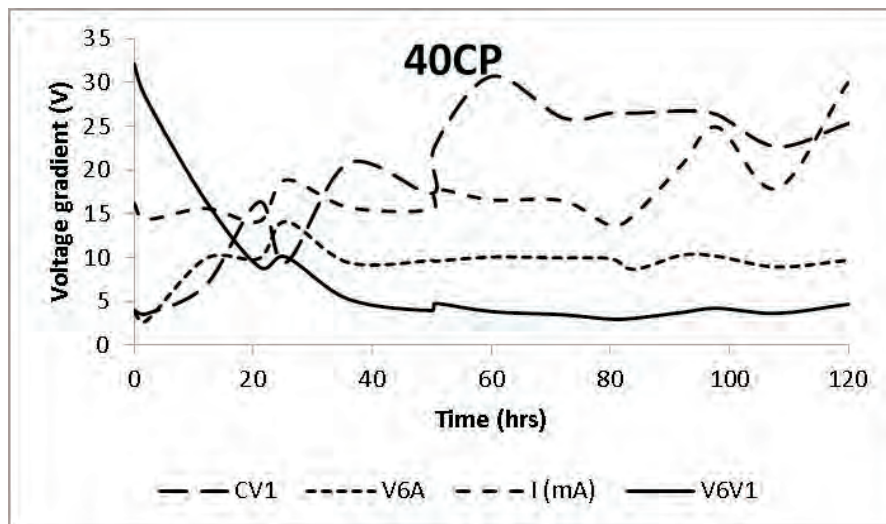Figure 8: Current Flow and Voltage across the Electrolyte (40NP)

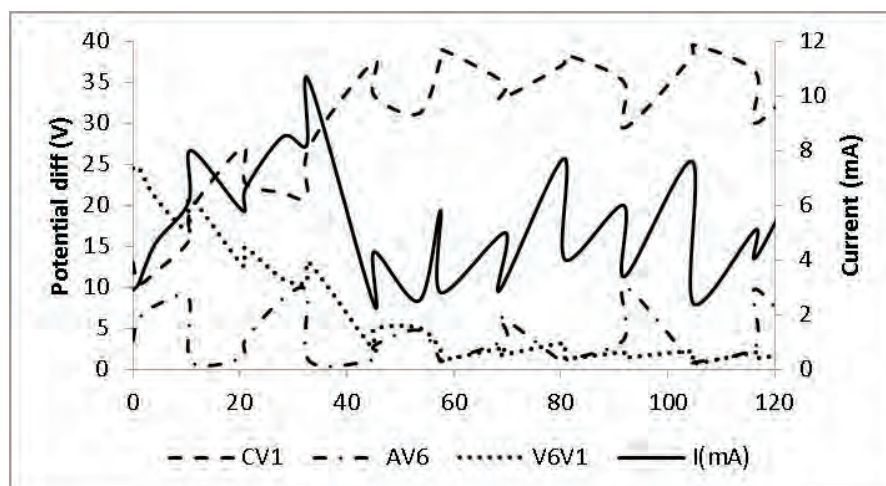Figure 9: Current Flow and Voltage across the Electrolyte (40CP

Figure 10: Current Flow and Voltage across the Electrolyte (40NCr)
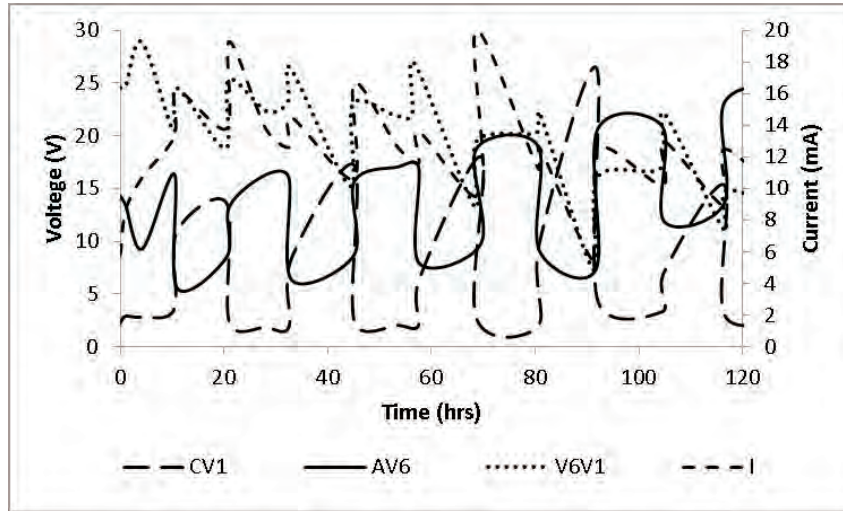
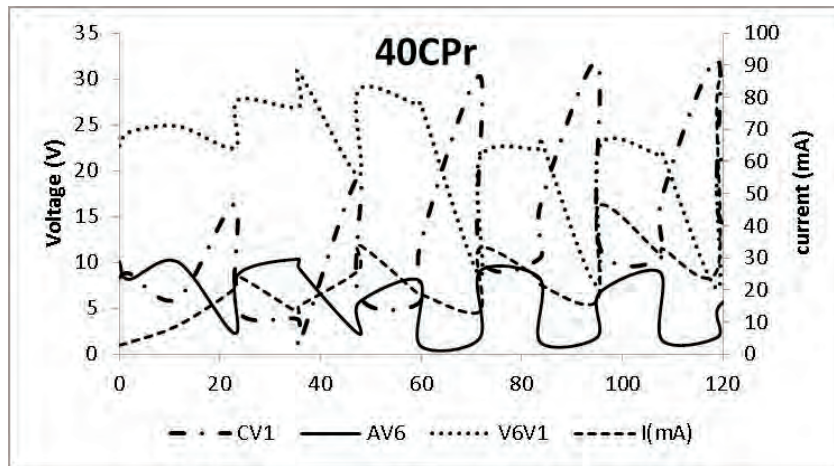Figure 11: Current Flow and Voltage across the Electrolyte (40NPr)

Figure 12: Current Flow and Voltage across the Electrolyte (40CPr)

Table 2: Effect of Selected Factors on Current during Treatment

Effect of Voltage				
	Degree of freedom	T Stat	P value	T crit
NP	29	12.245	5.54×10^{-13}	2.0452
CP	18	2.681	0.0152	2.1009
Effect of Polarity Reversal				
NC	63	21.854	4.17×10^{-31}	1.998
NP	76	7.349	1.92×10^{-10}	1.992
CP	24	1.970	0.0604	2.064

Table 3: Effect of Electrolyte on the Current

Source of Variation	Sum of Squares	Degree of freedom	Mean Square	F value	P-value	F crit
Between Groups	2435.799	2	1217.899	155.17	2.71×10^{-19}	3.238
Within Groups	306.0957	39				
Effect of electrolytes with Polarity Reversal						
Between Groups	43187.25	2	21593.62	83.893	4.1×10^{-26}	3.049
Within Groups	44014.5	171	257.3948			

Voltage Gradient within Treated Soil

The change in voltage gradient during the treatment process between the first and the last probe (V6V1 or V3V1) in the soil sample from cathode to the anode are presented in Figures 5 to 12. The potential differences between the probes were calculated by subtracting the voltage measured at a probe from that measured at the other probe. The results showed that the resistance of treated soil in tests NC kept reducing as the experiment progressed. This is because Ca^{2+} that migrated into the soil (and which remains in ionic form) increased the ionic content of the soil leading to higher conductivity of the soil and thus, lower potential differences. This is also revealed in Figures 13 and 14

The resistance of treated soil in tests NP and CP usually reduce as treatment progressed up to a particular time due to migration of ions into the soil. The resistance usually increased after the initial reduction, indicating possible precipitation of phosphate compounds at some limited area within the treated soil. The area of higher resistance was usually between the Middle and cathode sides.
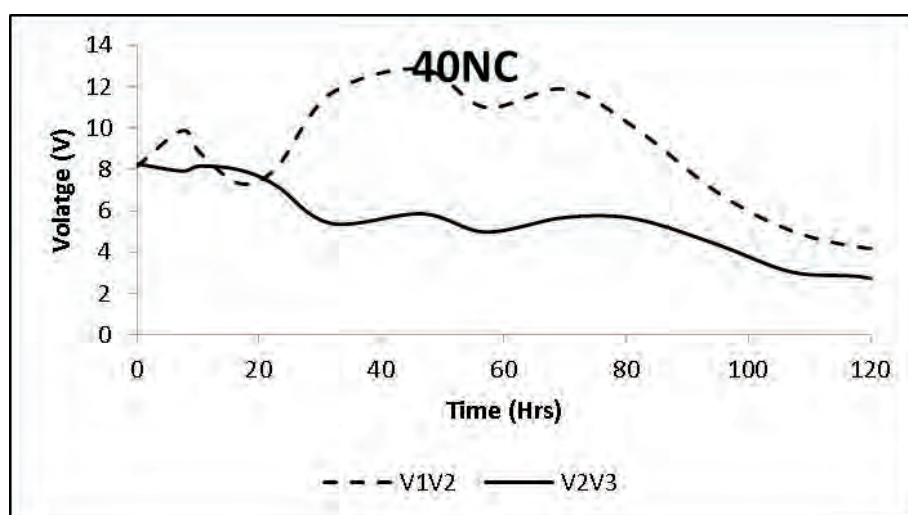

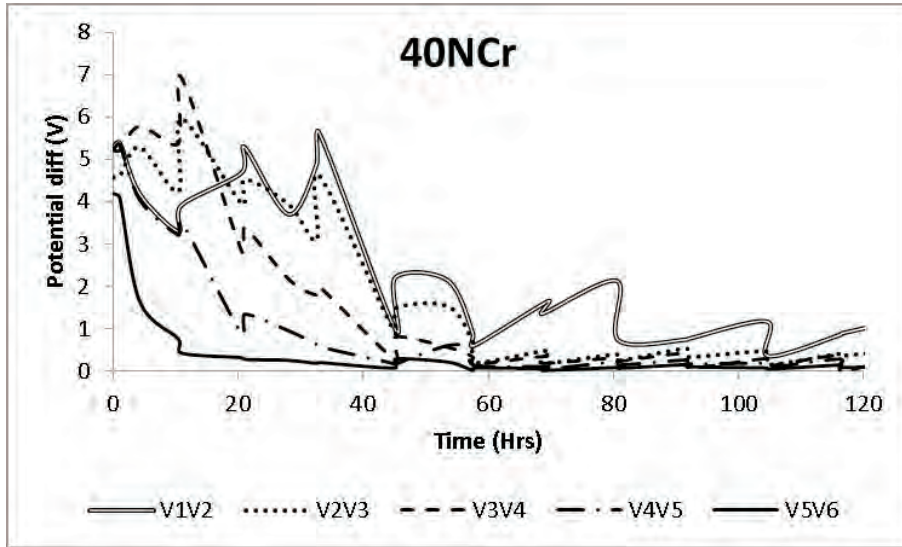Figure 13: Voltages within Treated Soil in 40NC

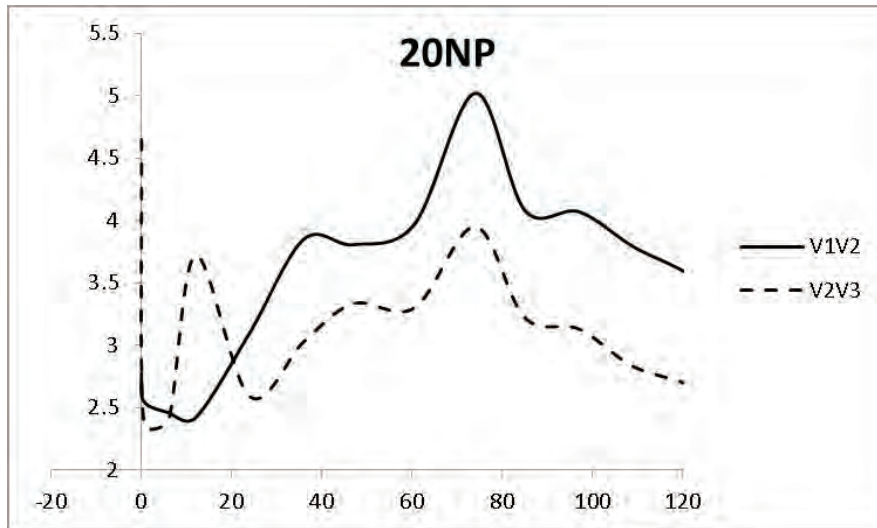Figure 14: Voltages within Treated Soil in 40NCr

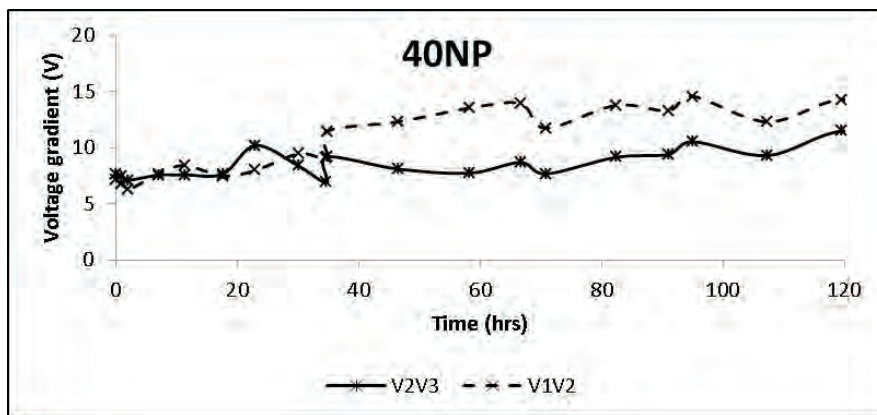Figure 15: Voltages within Treated Soil in 20NP

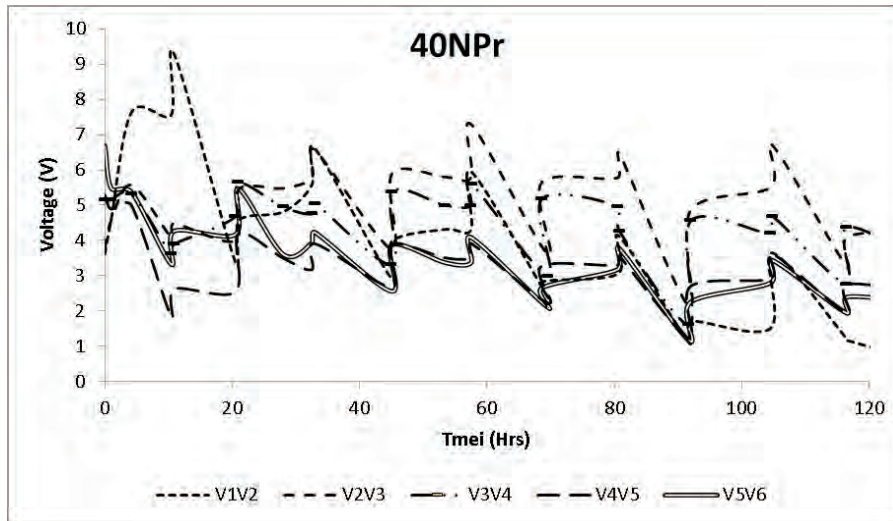Figure 16: Voltages within Treated Soil in 40NP

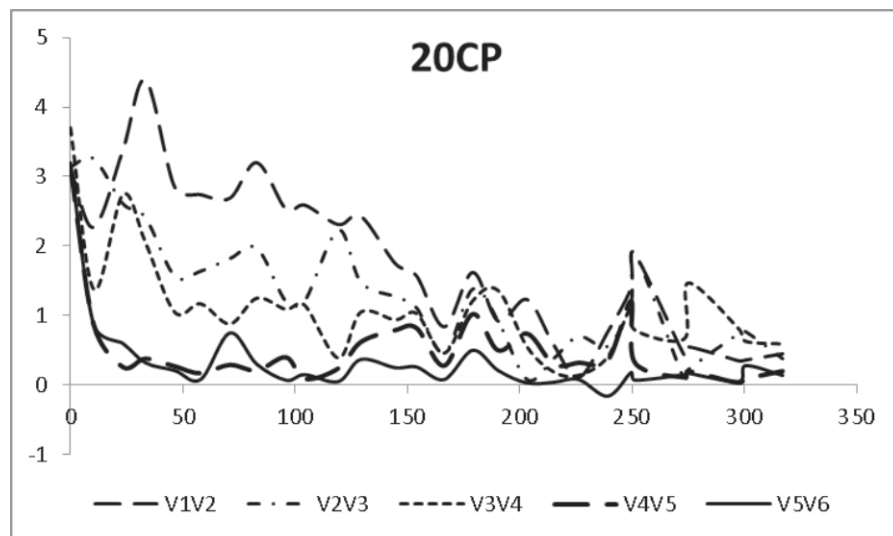Figure 17: Voltages within Treated Soil in 40NPr

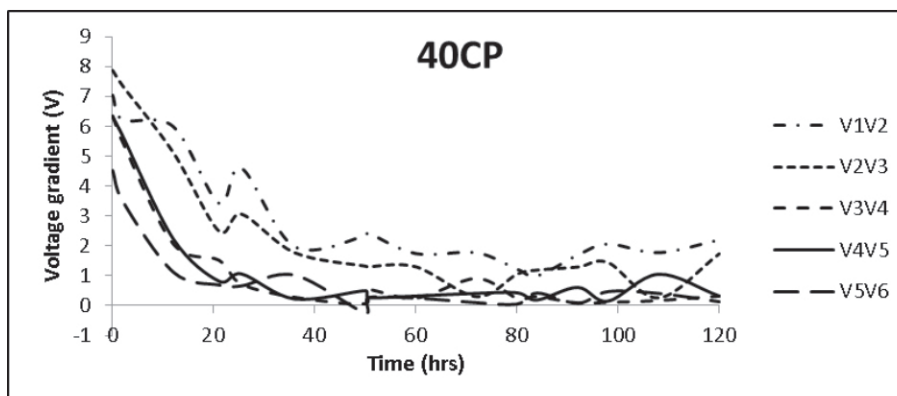Figure 18: Voltages within Treated Soil in 20CP
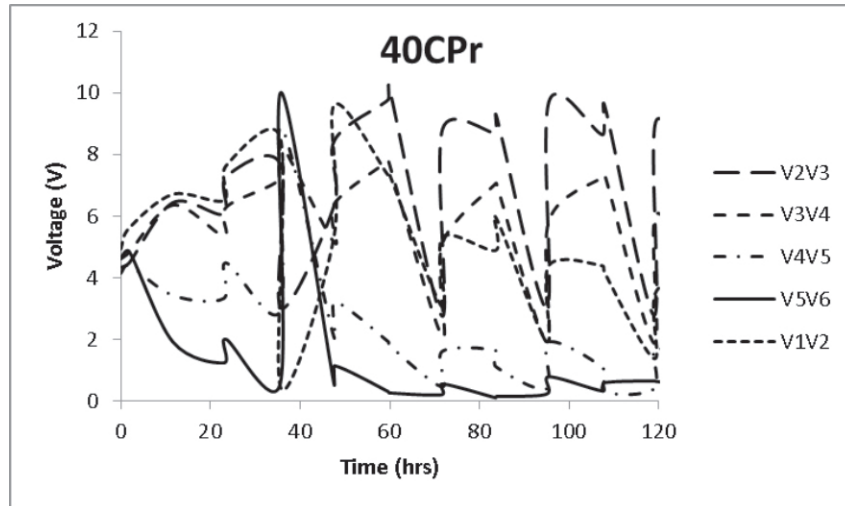

Figure 19: Voltages within Treated Soil in 40CP

Figure 20: Voltages within Treated Soil in 40CPr

Change in Electrical Conductivity of the Electrolytes

The conductivity of PA kept reducing as the experiment progressed while that of NaCl and CaCl$_2$ kept increasing as illustrated in Figures 21 and 22. The electrical conductivity of the catholyte is on the primary axis in Figure 21 while it is shown on the secondary axis in Figure 22. This behaviour shows that (according to McKinleyl and Savvidou, 1997), the electrical conductivity of an aqueous solution is a function of the nature and amount of the electrolytes present. Changes in the electrical conductivity can be linked to changes in the concentration of individual chemical species and vice versa. The ionic strength I$_s$ is given

$$I_s \quad \frac{1}{2} \quad m_i z_i^2 \qquad (3)$$

where:

I$_s$ is ionic strength; m$_i$ is molality of ion i and z$_i$ is charge of ion i.

The presence of other ions with which it interacts electrostatically affects the properties of an ion species in solution. The activity a$_i$ expresses the availability of the species to determine properties, to take part in a chemical reaction or to influence the position of equilibrium (Crow, 1994) and it is related to concentration c$_i$ as:

$$a_i \quad \tilde{a}_i c_i \qquad (4)$$

where:

a$_i$ is activity of ion i; γ_i is ionic activity coefficient of ion i and c$_i$ = concentration of ion i.

Using Kohlrausch's law of independent migration of ions, the electrical conductivity $\varkappa$ of the solution is presented as follows:

$$\hat{e} \quad \sum a_i \ddot{e}_i^* \quad \sum \tilde{a}_i c_i \ddot{e}_i^* \quad \sum c_i \ddot{e}_i \qquad (5)$$
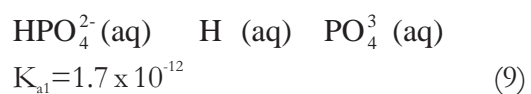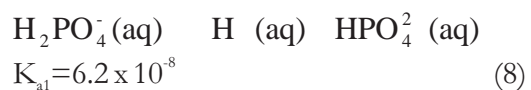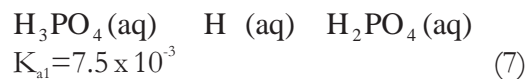
where:

$\varkappa$ is electrical conductivity V/cm; λ_i = ionic conductivity of ion i in water and λ_i^* = limiting ionic conductivity of ion i in water.

where λ_i^* is given as:

$$\ddot{e}_i \quad \tilde{a}_i \ddot{e}_i^* \qquad (6)$$

Increase in conductivity of NaCl and CaCl$_2$ electrolytes suggests that ionic content of these electrolytes were increasing as soil treatment progressed whereas reduction in the electrical conductivity of PA suggests reduction in ionic content.

Phosphoric acid is triprotic acid having three ionizable hydrogen atoms and its dissociation is 3-stage having different acid dissociation constants (K$_a$).

$$H_3PO_4(aq) \quad H(aq) \quad H_2PO_4(aq)$$
$$K_{a1} = 7.5 \times 10^{-3} \qquad (7)$$

$$H_2PO_4^-(aq) \quad H(aq) \quad HPO_4^2(aq)$$
$$K_{a1} = 6.2 \times 10^{-8} \qquad (8)$$

$$HPO_4^{2-}(aq) \quad H(aq) \quad PO_4^3(aq)$$
$$K_{a1} = 1.7 \times 10^{-12} \qquad (9)$$

The reduction in conductivity of the PA electrolyte also implies a reduction in the

concentration of ions in the solution. This can be explained as follows: the hydrogen ion released from the dissociation of PA was neutralised by OH⁻ ions generated due to electrolytic reaction at the cathode leading to a reduction in the ionic content of the electrolyte solution.
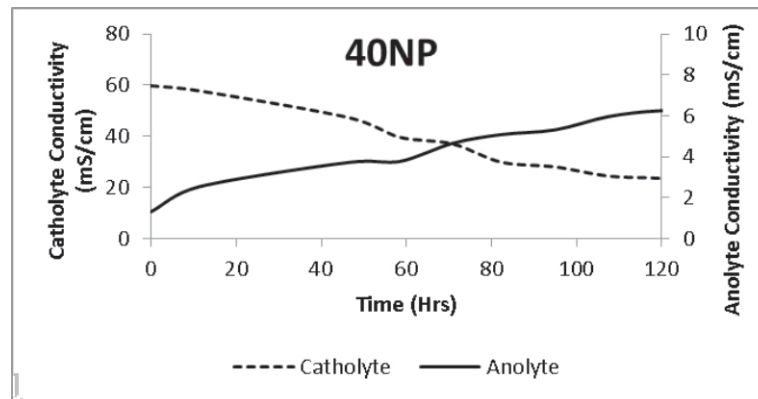

Figure 21: Electrical conductivity change on the electrolytes in 40NP
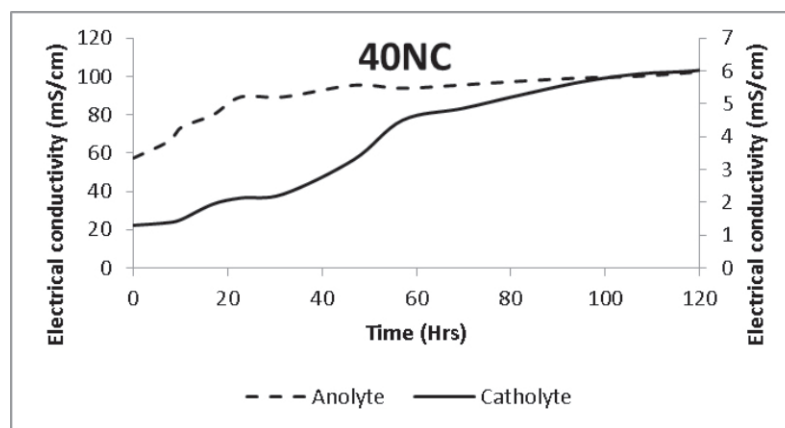

Figure 22: Electrical conductivity change on the electrolytes in 40NC

Energy Consumption Analysis

The electrical energy expenditure during each experiment was determined based on the soil electrical resistivity and the applied electrical potential are presented in Table 4.

Based on the power consumption analysis as well as the improvement recorded in the treated soil samples, it is not economical to use CP, even though higher current was generated but the resulting increase in soil properties does not justify the use. As earlier observed in the previous sections, the power utilised at the electrodes in tests CP and NC were higher than that utilised in tests NP. The power utilised at the cathode of tests 40NPr was however higher than that utilised at the cathode of test 40NCr due to reverse polarity.

The results further revealed that the use of PA as the catholyte is more economical than the use of the other electrolytes. Generally, the power consumption is minimal which implies that ECT is a feasible and economical option for in-situ stabilisation of soil.

CONCLUSION

This study has shown that both NC and CC behaved differently than PA when used as electrolytes in ECT of a laterite. While the electrical conductivity of both NC and CC increased during the test, the electrical conductivity of PA reduced. Despite the reduction in the electrical conductivity of PA, the electrical current generated in the system was higher than that generated in system consisting CC. Voltage losses at the electrodes were also

minimal in tests containing PA whereas high voltage losses were recorded in tests containing NC and CC. The applied voltage, polarity reversal and the type of electrolyte used are significant factors affecting the current and voltage loss during ECT, this findings were also confirmed by statistical analysis with P values of consistently less than 5%.

Table 4: Power Consumption during Experiment

Exp.	I_{avg} (mA)	Power Consumption (Watts)									Energy (Wh)
		P_{avg}	P_{CV1}	P_{V1V2}	P_{V2V3}	P_{V3V4}	P_{V4V5}	P_{V5V6}	P_{V3-A} P_{V6-A}	P_{C-A}	
20NP	1.059	0.021172	0.0052	0.0090	0.008	-	-	-	0.0142	0.0223	3.567
20CP	15.28929	0.288247	0.0915	0.026669	0.019088	0.0158	0.0078	0.0037	0.1221	0.2948	91.36
40NC	1.826	0.073031	0.033249	0.014434	0.009051	-	-	-	0.015961	0.072696	22.78
40NP	2.863	0.114532	0.008133	0.037315	0.023084	-	-	-	0.042008	0.110539	38.48
40CP	17.717	0.662878	0.356525	0.051053	0.04097	0.0192	0.0207	0.0136	0.1656	0.66767	222.73
40NCr	5.123	0.2049	0.1734	0.0086	0.0065	0.0051	0.0029	0.0012	0.0156	0.2134	68.55
40NPr	12.652	0.5061	0.0882	0.0288	0.0468	0.05151	0.0399	0.0422	0.226	0.5234	168.01
40CPr	42.13	1.6854	1.0539	0.1498	0.1731	0.1368	0.053	0.0224	0.1898	1.7042	566.35

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