CEE 281: Special Topics Report

Electrically Stimulated Recovery of Oil from Clay Rich Formations

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Abstract

This paper seeks to present and explain the observations and the results of a set of two experiments EK1 and EK 2, which were carried out to investigate the electrokinetic behavior of two clay soil cells that were purposely contaminated by refrigeration oil and natural oil respectively. Both soil formations were made from mixtures of clay silt and sand in the ratio of 2:2:6; however EK1 cell was measured to have 19% initial oil content, while EK2 was measured to have an initial oil content of 10.5%. These cells were subjected to a voltage gradient of 1.5 V/cm for 25 hours under recorded electrolyte pH and conductivity conditions.

The motive of this study was to investigate and quantify how well oil could be extracted from clay formations by electrokinetic methods. This information was derived from gravimetric analyses and presented in charts, but in addition other non gravimetric parameter data were also recorded, presented and discussed. These other parameters are pH, conductivity, current, voltage gradient, and flow rates, and they serve to indicate how much of the anticipated processes were occurring (current and flow), and what their effect on the soil's water content was, from the anode to the cathode.

The results show that significant amounts of oil (up to 50%) were removed from clay by the electrokinetic processes, as predicted by available literature; such as compiled by Environmental Protection Agency/Office of Radiation and Indoor Air/Center for Remediation Technology and Tools (EPA/ORIA/CRTT) in their resource guide- this guide lists all electrokinetic processes used on a patented, bench, pilot, field or conceptual scale from the period 1992 to 1997.[1]

The highest success rate was in the first experiment (refrigeration oil), which produced soil samples that contained an average of 12% less oil than the initial 19%, while the second experiment (natural oil) yielded an average of about 5% less oil content compared with the initial 10.5%. These results were obtained from gravimetric analysis.

1. Introduction

Electrokinetics (EK) is an umbrella term that refers to several physical and chemical processes that occur in a soil when it is subjected to an electrical potential. The processes vary, depending on the nature and the water content of the soil among other factors discussed in this report. The phenomena of electrokinetics have been studied by geotechnical engineers with the prospect of using them in the otherwise difficult remediation of oil-contaminated or heavy-metal contaminated clayey soil. This application of EK in soil remediation is known as electrochemical soil processing. Laboratory studies carried by geotechnical engineers such as Hamed and colleagues as well as Pamukcu and Whittle previously show electrochemical soil processing to be an effective method of lowering contaminant concentrations with a yield of 80 to 95 percent efficiency in the removal of some heavy metals such as Lead [2], Cesium and Strontium, as well as in the removal of some poly-aromatic hydrocarbons (oil constituents) from clays like kaolinite and montmorillonite.[3]

The positive results provided by these geotechnical researchers have stimulated the ongoing research into the field as geotechnical engineers in the field try to find ways of improving and modifying the process for higher yield, cost-effectively. EK technology holds the promise of an effective and highly affordable method of remediation of contaminated clay soils. The remediation of clays has been otherwise ineffective by conventional methods (such as in situ bioremediation and phytoremediation) due to the low hydraulic conductivity of clay, the generally higher cost of the alternatives.

2. Background

Electrokinetic processes key to this study and experiments are electroosmosis, electrophoresis, electromigration as well as ion exchange or oxidation and reduction reactions (redox reactions).
Electroosmosis is the movement of soil moisture or groundwater from the anode to the cathode of an electrolytic cell, while electrophoresis is the transport of charged particles or colloids due to the influence of an electric field. Electromigration, on the other hand, refers to the transport of ions and ion complexes to the electrode of opposite charge and it usually results in the occurrence of the mentioned oxidation and reduction reactions.[4]

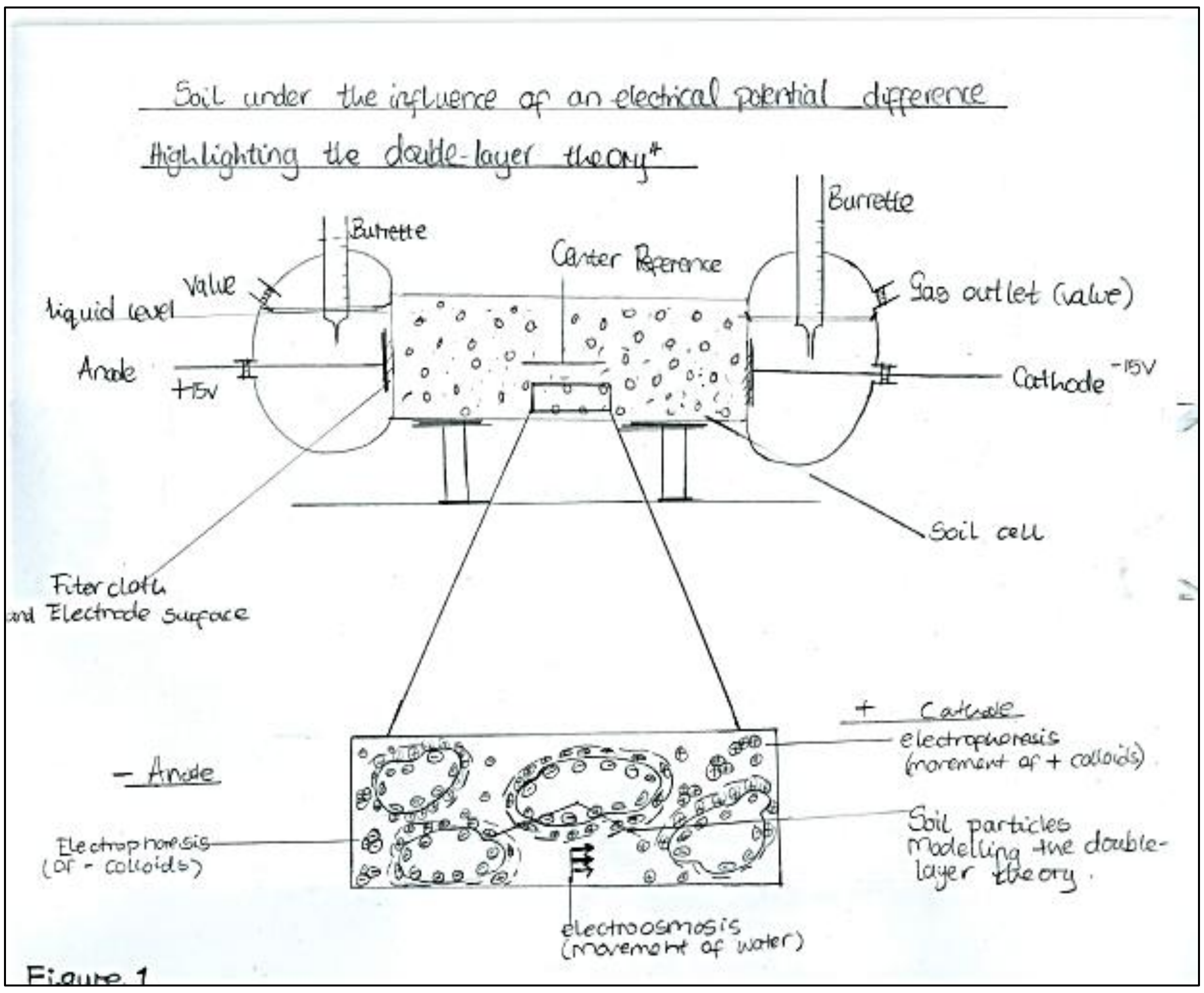

Figure 1.*Illustration of the double-layer theory*.

To explain the phenomena of electrokinetic processes in soil, Freundlich's double layer theory of soil water is used[5] . According to Freundlich, water immediately surrounding a soil particle is made of two layers, an outer layer, and an inner layer. The outer layer has an excess of cations (H^+) which are attracted to a negatively charged cathode, while the inner layer has an excess of anions (OH^-) which become attracted to the anode when a voltage is applied. Winsauer and McCardell identified that the surfaces of clay soils or colloidal materials tend to posses more anions than cations in an ionic solution. Due to the presence of these anions on the outer layer, the soil particles become negatively charged with respect to the solution and then they attract cations so forming a diffuse ionic layer[6].

Under the influence of the applied potential difference, cations and the organic compounds (oil constituents) are attracted to the cathode forcing the electrolyte and porewater flow towards the cathode, and drag attached oil droplets to all to the cathode.
This description and theory suggest that the major process in the electrokinetics of clay is electrophoresis, while the results from experiments, EK1 and EK 2 provide the relevant discussion data.

3. Methods

3.1 Preparing the Materials and Apparatus

The preparation of the formation soil was the first step in each experiment. For both experiments, kaolinite clay was used, mixed with sand and silt in the ratio of 2:2:6, toting up to a mass of about 300grams. The next step was the preparation of formation water by dilutions; the dilutions were started off by mixing a cup of tap water with commercial sea-salt and diluting until the conductivity was about 60 mS. The most significant and defining parameter of this solution was the conductivity, and in both of the experiments, the final conductivity of the formation water was maintained to a preset value of 58.3 mS. The pH was also measured and it was the same reading of 8 for both experiments.

The third step was the preparation of a soaking emulsion of oil and formation water. Oil was mixed into the water in the ratio of 1:1, about 40 grams of each measured (with refrigeration oil in EK1, then natural oil in EK 2), and then thoroughly mixed on a magnetic stirrer for 10 minutes to mix well. This emulsion and formation soil were mixed together (by hand and spatula) into a homogeneous consistency and sealed to let the oil absorb for 24 hours before packing into the electrolysis cell. At this point, the EK cell apparatus; the glass cell, reservoir bulbs, filter cloths, burettes, electrodes, voltmeters and ammeter were tested and made ready.

After 24 hours, initial measurements of the pH and conductivity of the soil were taken, and in addition to that, a sample of the mixture for gravimetric analysis was extracted. In order to measure the pH and conductivity of the soil, a sample 3 grams was extracted, mixed with 30 grams of water, and then stirred well on the magnetic stirrer to produce a homogeneous mixture from which the digital pH and conductivity meter-probes could read the values. For the gravimetric measurements, two samples were prepared and dried for 24 hours at 105 degrees Celsius to measure the water content and then for another 24 hours at 500 degrees Celsius to measure the oil content.

Next, the soil was packed, the mass of soil packed recorded, and the electrodes connected through one end of each bulb to the cell soil inter-phase (with filters closing in the soil between). Care had to be taken to make sure that the links between the filter cloths and electrodes were secure. The burettes that measured the flow rate were also connected, leveled with a plumb line and their joints sealed. This is all shown in the pictures Figure 2 and Figure 3.

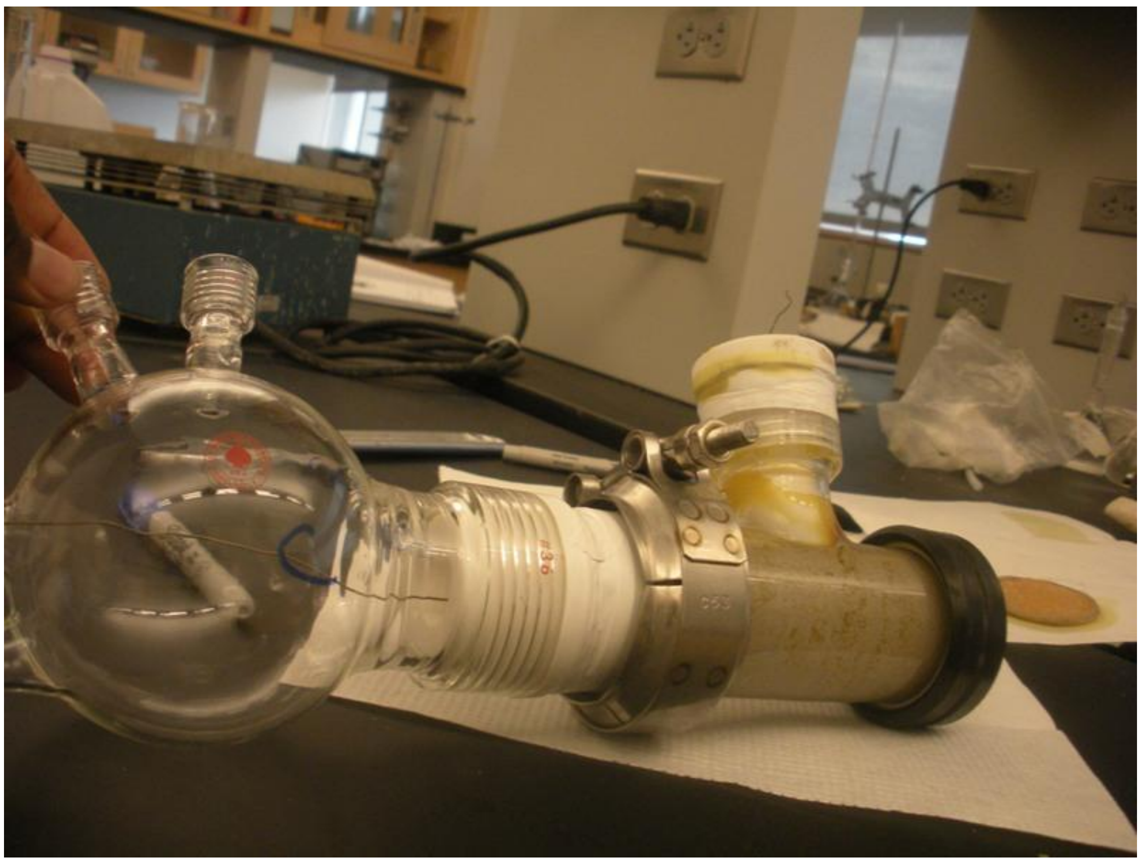

Figure2. ***Set-up of the cell.***

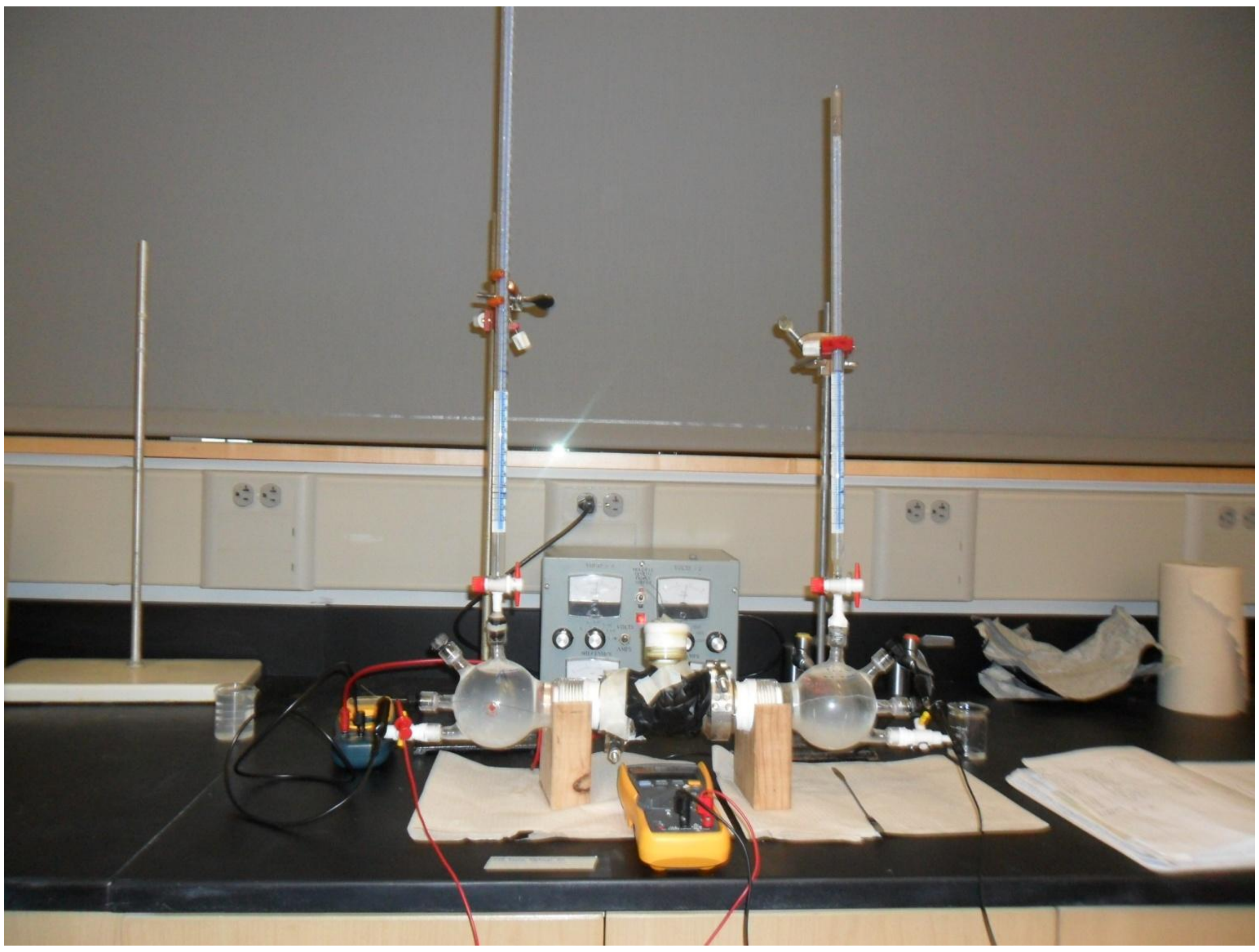

Figure3. ***Final station is set-up.***

An important part of this set up process was the sealing of the all the connections between the glassware. Careful sealing was crucial to secure against leaks, as gas, water and the water-oil mixture would leak at the slightest chance, altering flow readings. Silicone, Teflon tape, and rope caulk were used as sealants. When all was set, each of the reservoirs was filled with the formation water for 24 hours in turns in order to create some pressure hydraulic head, and saturate the soil formation.

3.2 Important Parameters and Data

Following the set up above, the system was ready for application of a voltage. In both experiments, the voltage applied across the cell was maintained at 15 Volts. This voltage was continuously applied for twenty-five hours in five hour sessions (for both EK1 and EK2) while the parameters explained in the following paragraphs were tracked and recorded.

It is important to note that in the first hour, all these parameters were measured and recorded at five minute intervals to ensure a smooth start then every hour from then on as described.

3.2.1 PH and Conductivity

While the final results presented by the graphs show the changes in pH and conductivity of the soil after it was treated with EK, these parameters were also tracked and tabulated prior to and after every five hour session. The changes in the pH occur as a result of redox reactions. In compliance with Freundlich's double layer theory discussed earlier[5]; the outer layer of water consists of free H^+ ions that are drawn to the cathode. Here these hydrogen ions are reduced to hydrogen gas increasing the pH, and as follows:

$$2H^+ + 2e^- <=> H_2 \quad (1)$$

As a result of this reaction, the pH values at the cathode were high, with values ranging from 8 to 11 and the end of each of the five EK sessions.
At the anode, the opposite occurs as water molecules are oxidized into oxygen gas and H^+ ions according to this reaction:

$$2H_2O <=> O_2 + 4H^+ + 2e^- \quad (2)$$

These redox reactions result from the electrolysis of water. When electricity is passed through the soil, H2O is split into H+ and OH- ions, OH- ions are attracted to cathode, hence high pH. On the other hand H+ ions are attracted to anode, hence low pH.
In confirmation with the theory, the measured pH at the anode was acidic, with values ranging from approximately 6 to 2 for both tests while the pH at the cathode was basic, with an 8 to 12 range. These values are significant as they indicate that the redox reactions were occurring in the system. At this juncture, it is necessary to mention that the low pH environment weakens metals and hence the anode had to be tested before every test to make ensure that it was not broken or too weak to prevent it from shorting the circuit as the test ran.

The conductivity of the electrolyte at the beginning and end of each five hour session was also measured and tracked in order to follow changes in the electrolyte oil content from the anode to the cathode. Interpretation of the readings is based on the rationale that when the concentration of oil droplets in an oil-water emulsion is high, the emulsion conductivity falls, and vice versa. With this information we are able to understand that direction of electrophoresis was from anode to cathode as predicted, because conductivity readings fell from anode to cathode. The electrolyte conductivity was measured from reservoir extracts of 10cm^3 diluted to a 100cm^3, such that our regular low range digital meter gave off the reading with a factor of 10.

3.2.2 Current, Flow and Gas

The current and the flow through the cell were measured every thirty minutes from the second hour because they served as important indicators of the progress and the magnitude of the EK processes that were occurring in the cell. If the current was consistent, then the redox reactions, electrolysis and electromigration and flow rates within the closed system were also smooth. It is also important to note that a sample of the electrolyte from each reservoir was extracted for analysis at the end of each test. Formation water was replaced in each reservoir to measure the concentration of hydrocarbons for the purpose of analyzing oil removal from the soil formation. After extracting samples for analysis in-between applications of current, the reservoirs were refilled to maintain saturation of the formation soil. Current measurements were read off a digital ammeter that was connected in series with the cell circuit, while flow and gas measurements were tracked by recording changes in the burettes' volumes and by careful control of reservoir valves that released the gas every half hour.

3.2.3 Voltage

Voltage measurements were recorded every hour to ensure that they were consistent. The voltage gradient was maintained at 1.5 V/cm, - The voltage gradient between the anode and the middle of the cell was measure to be approximately 1 V/cm and between the middle and the cathode approximately 0.5 V/cm. The importance of the potential difference lies in that the there is proportionality between the electroosmotic velocity of the water through the soil and the voltage gradient $\Delta V/\Delta X$, such that the EK flow can be expressed by the following equation; (3) , which was developed by Yeh and Wu: [7]

$$U = Q/A = K\ \Delta V/\Delta X \tag{3}$$

Here, U is the electroosmotic velocity, K is a constant, coefficient of elctroosmotic permeability and a soil property, Q is the flow, and A the cross-sectional area of the cell. From this equation, we understand that the voltage gradients from either electrode to the center of the cell need to be relatively consistent for a smooth rate flow.

The above data, which was extracted during both EK1 and EK2, is presented in Table EK1 and Table EK2 and corresponding graphs are available in the appendix for the reader for the reader.

4. Results Analysis and Discussion

After twenty five hours of EK, the tests were stopped and the soil prepared for analysis. This analysis was carried out on samples extracted from the soil cell lengthwise from the anode to cathode. In order to extract these samples, the five 2cm graduations were measured off on the 10cm glass cell from the anode to the cathode, and the five soil samples scooped out, carefully working from the anode to the cathode into five dished labeled 1-5. To reiterate; the 2cm length of soil closest to the anode became sample 1, and the second 2cm became sample 2 and so forth.

The five soil samples being tested for pH, conductivity, water content as well as oil content patterns from the anode to the cathode. This data was plotted against normalized distance from the anode, and it is compared and discussed below.

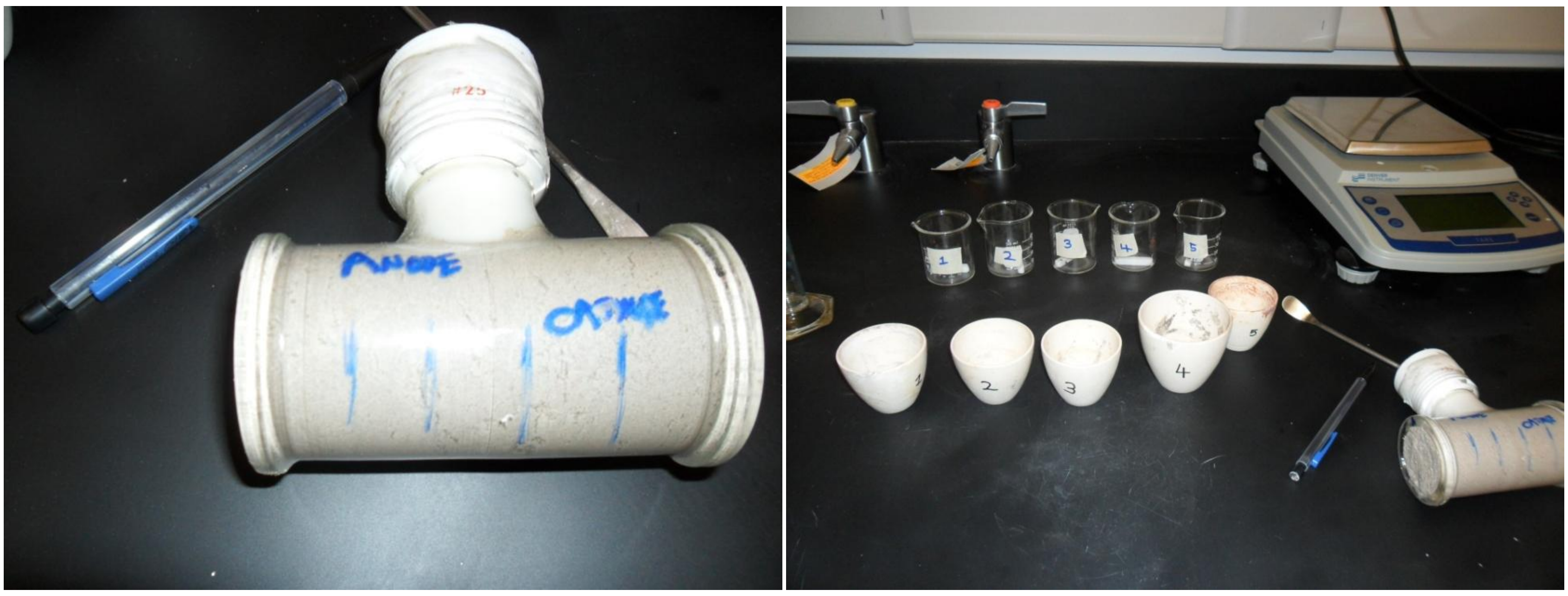

Figure 4. Figure 5. ***Preparation for Post EK analysis.***

4.1 PH and Conductivity

The pH and conductivity versus normalized distance from the anode graphs for EK 1 (test performed on clay- refrigeration oil mix) are shown in Figure 6 while those for EK 2 (test performed on clay-natural oil mix) are shown in Figure 7.

Both graphs display a steady increase in the soil pH from the anode to the cathode with minimums of 5.5 and 4 for the samples right next to the anode, and maximums of about 6.5 and 7 at the cathode- EK1 then EK2 respectively. The slight difference could be due to the different types of oil used; however the trend is the same- the soil pH are low at the anodes, and high at the cathode as anticipated by the equations 1 and 2.

On the other hand, the trends in conductivity do not all follow any prediction (which would be that conductivity falls consistently towards the cathode). Figure 6 (EK1) shows that the readings of conductivity generally started off low for the first two samples then they raised for the three samples following. When compared with the final gravimetric data this is agreeable because the oil content increased more significantly for the first two point (0-4.5cm of the cell). Figure7 (EK2) on the other hand, follows the prediction, showing that the conductivity falls towards the cathode, indicating a higher concentration of oil at the cathode, and confirming the theory.

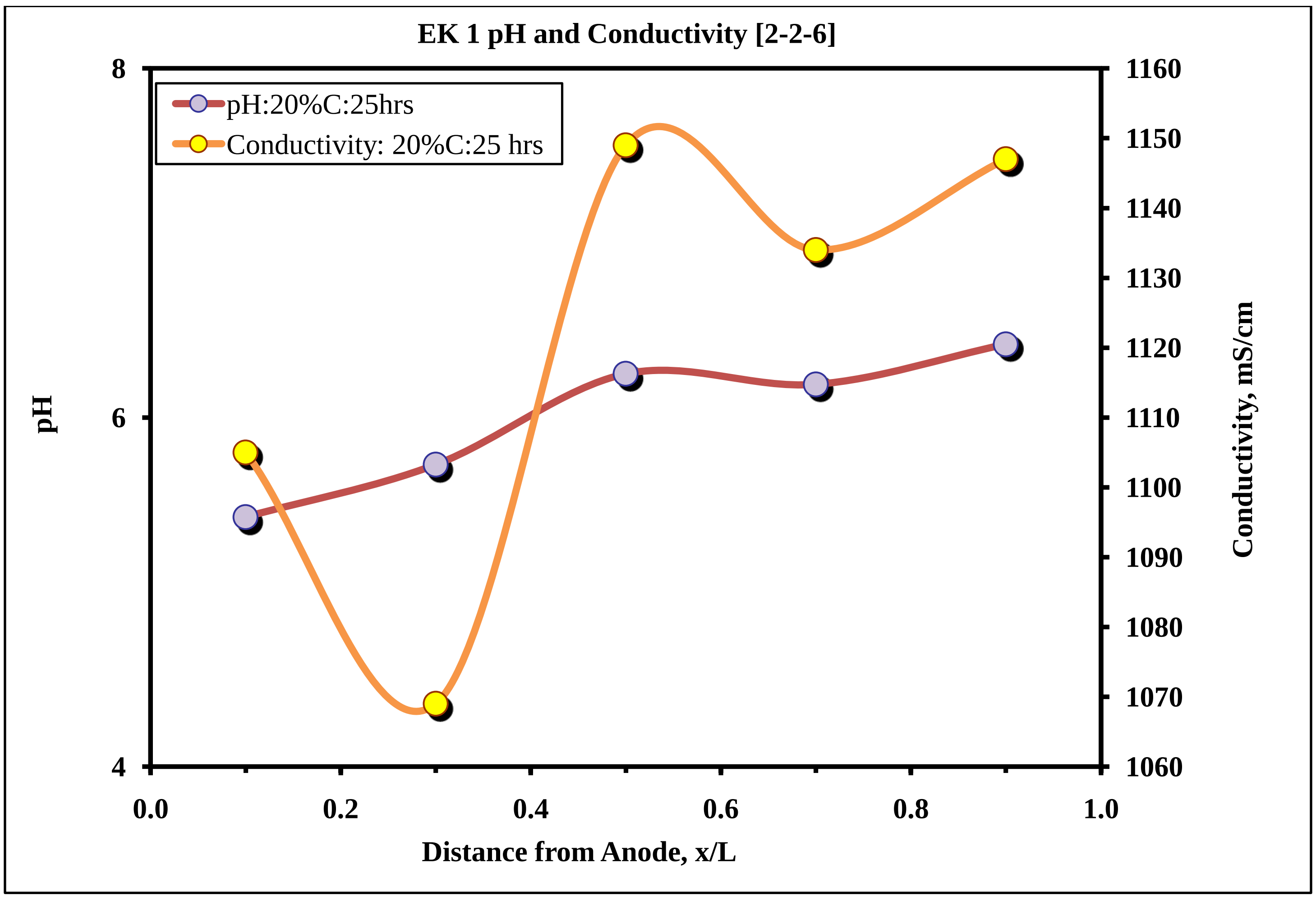

Figure 6. EK1. ***Post EK pH and Conductivity Curve.***

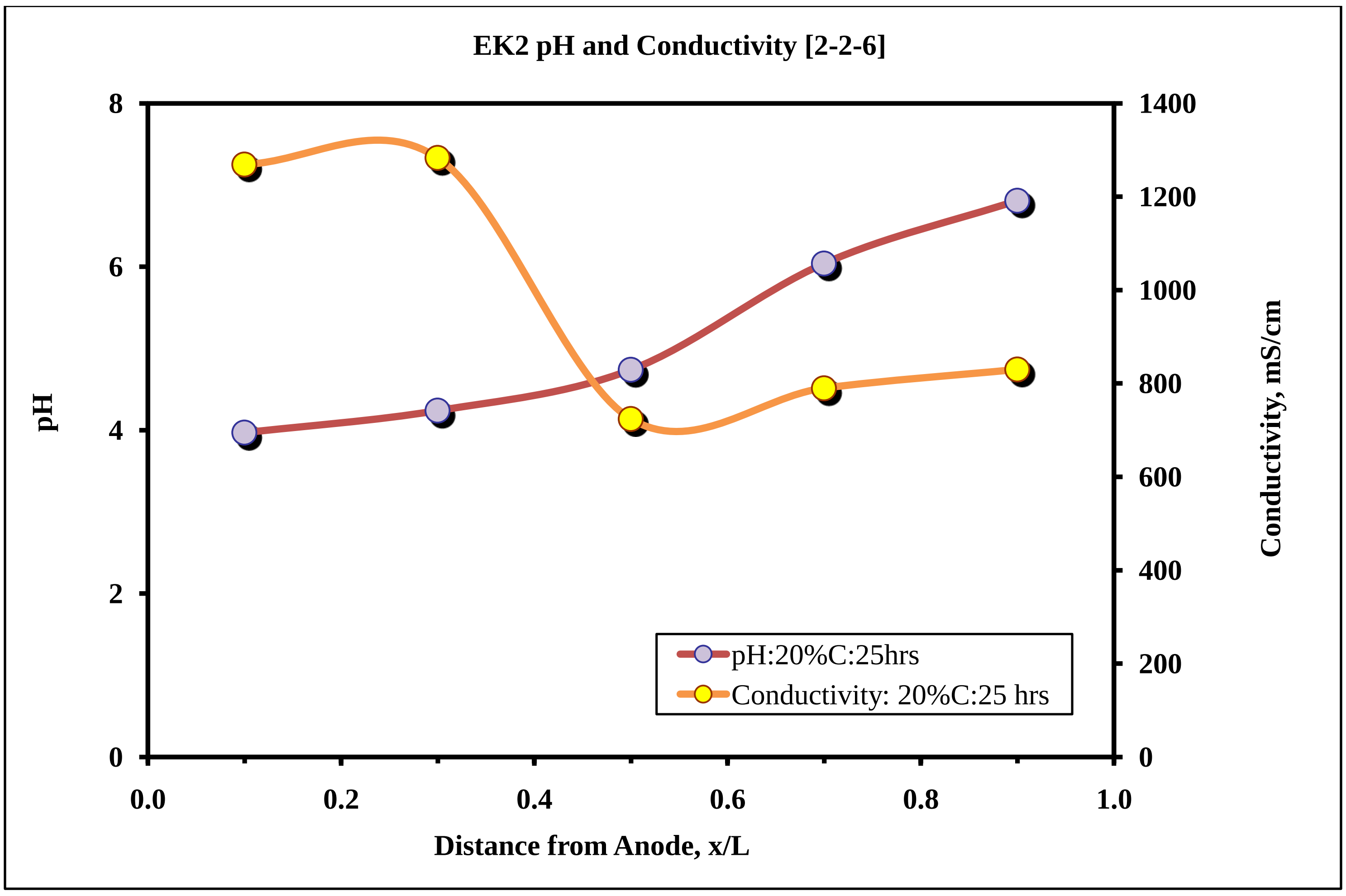

Figure 7. EK2. ***Post EK pH and Conductivity Curve.***

4.1 Oil Water Ratio

Gravimetric analysis was carried out on the five samples from each experiment and the oil and water content values were determined and also plotted against distance from the anode Figure8 and Figure 9. These O/W ratios show that there is a significant decrease in the initial O/W ratio of the soil from the pre-EK samples to the final set of five extractions. There is also further decrease in the O/W ratio for both extracted samples from the anode to the cathode. These trends are in agreement with the desired outcome from EK, the decreasing O/W ratio shows that oil were moved from the soil cell, with increasing amounts from the anode to the cathode.

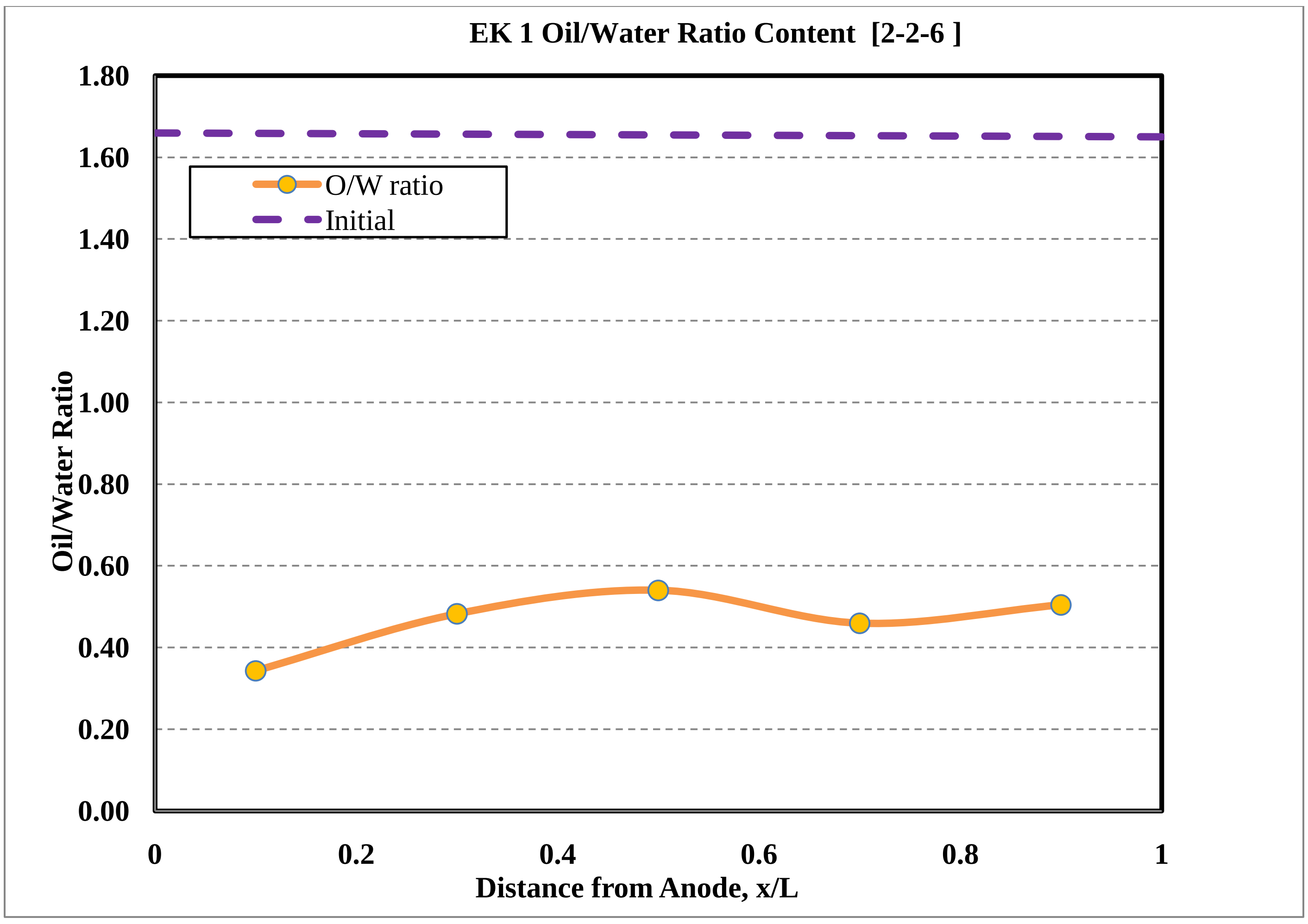

Figure 8. EK1. ***Post EK Oil/Water Ratio Curve.***

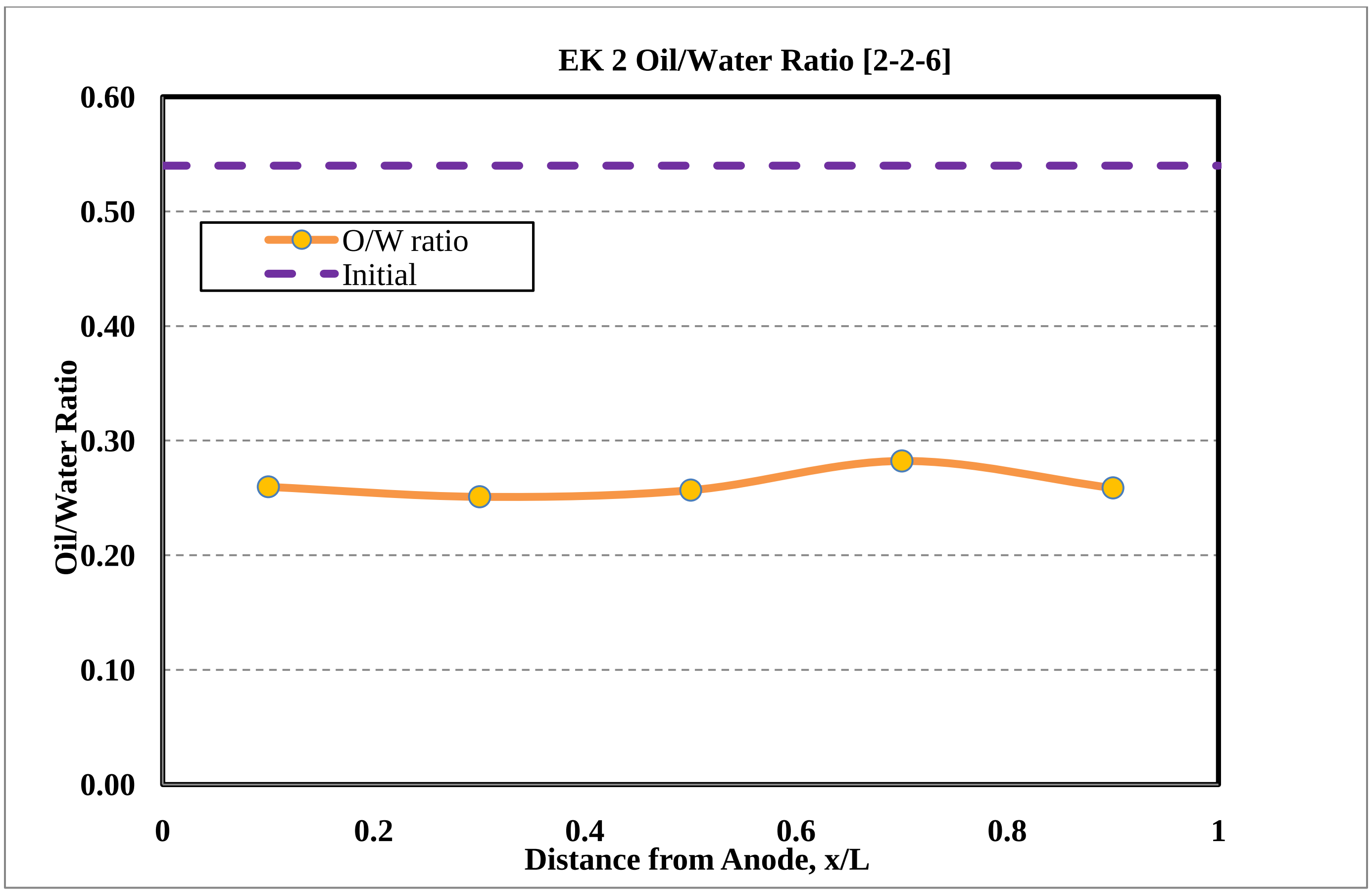

Figure 9. EK2. ***Post EK Oil/Water Ratio Curve.***

5. Conclusions and Comparisons

The results and experimental data discussed above are in agreement with the results from the ongoing research on EK that is available from already published library material (used in the background). The tests reported here do confirm that electrokinetics can be used to effectively remove oil from clays.

The differences, however, are in that EK1 and EK2 were relatively short and hence they may not compare with some documented tests in efficiency (some of these went for months on end). Since the extraction of oil is cumulative, a longer process is likely to extract a higher amount of oil from the soil, and register a higher efficiency of the process than a short process.

Second EK1 and EK2 were also unique in that they were carried out using commercial clay, and soil and formation water prepared to model the actual field clays. Most of the documented tests were carried out in real soils in no isolation from natural forces, in situ, and hence they produced real field results. Nevertheless, these experiments were relatively successful, with only a few challenges that are addressed in section 6.

Between the two of them, EK1 and EK2 also show significant differences in their raw data- flow, pH changes as well as gravimetric results. EK2 has a higher net flow values (35ml) while EK2 has a net flow of about (32ml) at the 25th hour. This is a trend that follows the trend in their respective current readings- EK1 has higher current readings than EK2 and there trend are consistently the same with the Voltage gradients. These differences are only in the running of the electrokinetic experiments. After data was analyzed however, the general result is the same, oil moves from the anode to the cathode. Further tests[8] on the anolyte and catholyte by the Extraction and the TOC methods also show confirm the consistency of the result.

6. Sources of Error, Experimental Challenges and Suggestions For Improvements

6.1 Errors

The most obvious experimental challenge and source of error was in the measurement of volumes, especially the gas volumes. The burettes are very sensitive instruments; the changes in volumes as a result of gas production were more sensitive. A very small change in the level of the electrolyte signified a large volume of escaping gas, and this was difficult to measure accurately measure. In the second test EK2, a whole session of readings (the last five hours) was thrown off because the reservoir datum could not afford space for the gas produced; resulting in continual leaks between volume readings and the datum had to be reset. –The datum had to be reset because the working datum was too low for the flow of gas to cause measurable burette changes.

The second major source of error was in the form of losses in oil to the glassware and also in the form of leaks (leaks during packing). The absorption of natural oil was actually so low that it was recorded in the picture below- Figure 10 and figure 11. It should be noted that this particular loss in oil is important because it occurred after the gravimetric sample was extracted, meaning that the measured initial O/W ratio is presumably lower than actual.

Figure.10, Figure.11 ***Oil seeping out of oil and losses to the filter during set up (this is after the initial O/W ratios were measured)***

Finally, errors occurred due to regular leaks as the sealant wore out or the connections (valve, burettes, rubbers, reservoir bulbs etc) shifted. This is a major challenge because the set up has many valves and connections. The only way to deal with leaks was to dry them up and seal them again, and, sometimes the entire burette set-up had to be redone, this was time consuming.

6.2 Suggestions for Improvements

According to several literatures, especially those of Yeh and Wu and Haran[9], pH control is a very important in clay electrokinetics. The findings of Haran state that the pH at the anode becomes more caustic as the EK progresses and this hampers the generation of the Hydroxyl radicals that push the equilibrium of equation 2 (anode reaction) forward, so, in order to avoid this and encourage faster rates of reaction and flow the electrodes can be made to alternate before each run, switching the electrodes prevents either one from extreme exposure to its default p.H condition (prevents the anode from becoming too caustic) and so maintaining dynamic the equilibrium.

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