

Electro-Deposition of Asphaltenes from Abu Dhabi Crude Oil/Synthetic Formation Water Mixtures

Hadil Abu Khalifeh¹ and Hadi Belhaj²

Abstract In this work, asphaltenes precipitation and deposition induced by applying an electric field to Abu Dhabi crude oil sample were studied. The asphaltic particle electrical charge and asphaltic deposits mass at different operating conditions were determined. Direct current (DC) was applied between two graphite electrodes dipped in crude oil/synthetic formation water mixture of 240K ppm salinity. Three current densities of 10, 20, and 30 A/m² were applied. Deposits were collected on the electrodes surfaces and their mass was recorded using low capacity load cells (up to 50g).

Anodic and cathodic deposits were observed at different operating conditions. The results revealed that asphaltic nature deposits were detected on the anode. The mass of deposits on the electrodes increased with experiment time and current density. With higher current density at experiment times below 10 hrs, the rate of the mass increase was faster. No charge alterations noticed with increasing run time and current density. Experiments showed that the maximum amount of asphaltic material arrested on the anode was 18% of the original asphaltic material in crude oil sample for current density of 30 A/m² and 24 hours run time.

Eventually, an asphaltene preventive/minimizing criterion can be set to combat deposition during production and enhanced oil recovery processes.

Keywords: Electrodeposition, asphaltenes, precipitation, electric charge, electric field, crude oil

1 Introduction

Asphaltene colloids are kept in suspension in the oil by the resins [Andersen and Speight (2001)]. The stability of asphaltene with resins can be altered by changing the prevalent crude oil chemical composition, pressure, and temperature. Several studies have reported that nature of asphaltenes and the dispersion medium have a strong impact on the stability of crude oils [Hammami et al (1998); Alkafeef (2001); Goual and Firoozabadi (2004)]. For example, [Hammami et al(1998)] has mixed two resins in different proportions with original oil. Then the mixtures were tested for asphaltene precipitation due to n-C₅ addition at 25°C and 690 kPa. They observed that the presence of a component may be responsible for asphaltenes stability only if another component (not necessarily a resin) was also present. Different resins were used to investigate resins effect on asphaltene precipitation by [Goual and Firoozabadi(2004)]. Three different petroleum fluids were mixed with various resins

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and precipitation with n-pentane was tested. Results revealed that the polarity of resins had a significant effect on precipitation and stability. The stability of asphaltene suspended in oil by resins is related to the electrical characteristics of asphaltene, resins and the remainder of the crude. The mechanisms of asphaltene dispersion and deposition need to be understood to improve remediation and prevention methods.

During exploitation and production of oil reservoirs, asphaltene deposition is always a huge challenge. Asphaltene deposition can occur during natural depletion, oil transportation, and during miscible and immiscible flooding operations [Hosseini et al (1997); Srivastava et al (1999); Jamaluddin et al (2002); Nghiem et al (2001)]. Remediation methods are implemented to remove the damage such as flow assurance problems, conduit clogging, pipeline plugging, and heat exchangers fouling. A clean-up of asphaltene deposition in onshore fields in Abu Dhabi using organic solvents and coiled tubing unit costs US \$200,000 [Misra et al (2013); Abdallah (2012)]. Therefore, alternatives to mitigate or prevent asphaltene deposition are required by Petroleum industry.

Using electrical potential is one of the promising approaches to enhance oil recovery and control asphaltene deposition. Oil recovery can be enhanced by applying an electrical potential difference between a producing well and electrode well [Eow et al (2001)]. Also, electrical means have been involved in technologies to solve problems such as streaming potential induced by the oil flow [Aggour and Muhammadain (1992)].

Electrodeposition is one of the techniques that employed an electrical potential to investigate current asphaltene particle charge and deposition kinetics. Electrodeposition is defined as the process of inducing oil components to deposit on one of the electrodes when an electrical potential is applied [Preckshot et al (1943); Moore et al (1965)].

[Hashmi and Ghosh (2015)] have conducted electrodeposition experiments to study asphaltene deposition from heptane diluted crude oil using a DC power supply. Results showed that applying electrical potential has increased asphaltene deposition on the anode.

The effect of high voltage direct current on asphaltene deposits size and deposition rate from three different crude oil samples mixed with toluene and n-heptane was investigated using electrodeposition by [Hosseini et al (2016)]. A high resolution optical microscope was utilized to monitor asphaltene particle size and aggregation rate. They reported that the electric field strength affected the aggregate size and aggregation rate.

Researchers found that the most polar asphaltene in crude oil deposit on the walls of tubing and process equipment [Gawrys et al (2003); Dubey and Waxman (1991)]. In addition, [Wattana et al (2005)] reported that larger portions of the higher polar fractions were in the asphaltene that were extracted from unstable crude oils compared to the asphaltene obtained from stable crude oils. Therefore, asphaltene deposition is controlled by polarity and charge of asphaltene.

Researchers have used electricity in lab scale since 1945. A lively debate among researchers regarding asphaltene electric charge is still on. Some researchers claimed that asphaltene is positively charged [Katz and Beu (1945); Dykstra et al (1944); Eldib (1962); Taylor (1998)], others conversely considered asphaltene particles to be

negatively charged [Khvostichenko and Andersen (2009); Hashmi and Firoozabadi (2012)].

The mechanisms that produce the asphaltene surface charge and factors that impact the charge need to be investigated to predict deposition tendencies from crude oils.

At the present time, very limited information is available on asphaltene deposition kinetics from actual crude oil samples under the influence of a DC current. This can be possibly because of the difficulty in using a technique to evaluate the kinetics. The aim of the present study is to investigate the charge and kinetics of asphaltene deposition from Abu Dhabi crude oils at various operating conditions under the influence of electrical potential difference.

2 Methodology

The experimental setup is shown in Figure 1. A 2000 ml cylindrical container holds two electrodes immersed in the mixture sample in the container. The mixture sample is composed of crude oil and synthetic formation water. A DC current is applied between the two electrodes immersed in the mixture. The two cylindrical electrodes have a length of 10-15 cm and 10 cm apart. A Direct Current (DC) is generated by electric power supply obtained from B&K Precision (model no. 9185). A load cell obtained from Futek Advanced Sensor Technology (LSB 200, Ultra low capacity 50 gram, resolution 0.000033 g) is used to record the change in the mass of the suspended electrode with real time. The setup is contained in a transparent plastic box to isolate the system from the surroundings. The data is collected and analyzed by SENSIT Software obtained from Futek Advanced Sensor Technology. Microscopic imaging for oil samples was performed with a digital microscope with a magnification of 3000X.

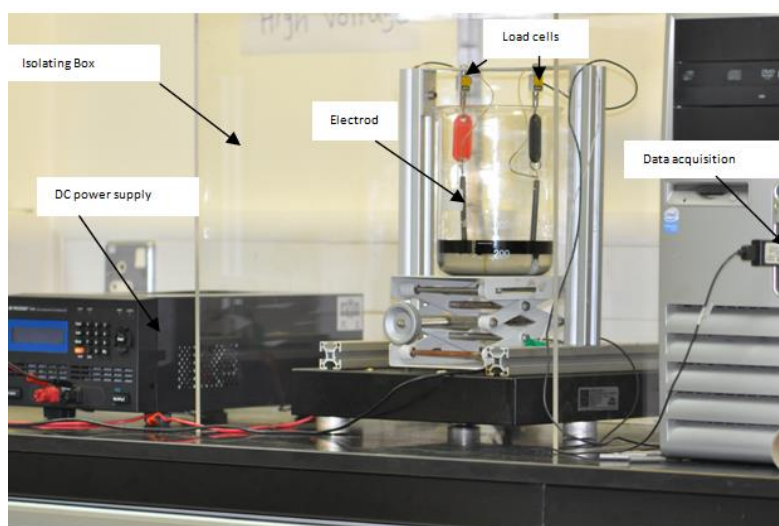


Figure 1: Experimental Setup

Crude oil was used in the experiments described in this work. Crude oil was dead oil obtained from Abu Dhabi fields. Data on Oil is given in Table 1. Resistivity for crude oil was determined by measuring the applied voltage and the corresponding electric current. A series of electric current measurements were performed on the sample by applying potential differences from 10 Volt to 620 Volt at room temperature. The

electric current at each potential difference was recorded by a multimeter and plotted as a function of voltage. Based on the data obtained, the resistivity of neat crude oil was calculated to be $25.32 \times 10^6 \Omega\text{m}$ (conductivity is $3.949 \times 10^{-8} \text{ S/m}$).

Table 1: Data for crude oil

| Components | Mole% |
|-------------------------|--------|
| C1 | 0.00 |
| C2 | 0.00 |
| C3 | 0.12 |
| i-C4 | 0.14 |
| n-C4 | 1.10 |
| i-C5 | 1.30 |
| n-C5 | 2.09 |
| C6 | 5.38 |
| C7 | 9.64 |
| C8 | 10.56 |
| C9 | 8.78 |
| C10 | 8.18 |
| C11 | 6.66 |
| C12+ | 46.05 |
| Molecular Weight(g/mol) | 187.38 |
| Density@60F(g/cc) | 0.84 |
| API Gravity | 36.7 |
| Saturates(wt%) | 68.9 |
| Aromatics(wt%) | 21.8 |
| Resins(wt%) | 7.1 |
| Asphaltenes(wt%) | 0.5 |

The formation water was synthesized in the lab to represent reservoir formation water. The runs were conducted with 240 K ppm formation water. The Physical properties for formation brine at ambient conditions are listed in Table 2. The ratio of oil to formation water of the sample mixture was 40: 60.

Table 2: Formation water Properties

| Property | Value |
|------------------|-------------|
| Density(g/cc) | 1.1625 @21C |
| Specific gravity | 1.1646 |
| pH | 5.92 |
| Viscosity(cP) | 1.91 |

The current density applied to the electrodes was 10, 20, 30, and 40 A/m² respectively. The load cells were recording the change in mass of electrodes for each run time interval.

An experimental program is constructed to determine the type of electrical charge asphaltene possesses in Abu Dhabi crude oils by applying electrodeposition approach. This is found by predicting the charge of the particle when it deposits on the

oppositely charged electrodes. In the experiments, current density: 10, 20, and 30 A/m² for 30 min, 1, 5, 8, 16, 24 hrs were applied. All experiments were conducted at room temperature (23°C±0.1) and room humidity of 50%. After completing the tests, the electrodes were taken out of the container and inspected for electrodeposition and left to dry through the night at room temperature (~21°C). The anode was washed with a solvent (Toluene) to collect the deposited material for further analysis. The material on the other electrode was left to dry and preserved for further analysis. The weight of deposited material was calculated by finding the difference of the weight between the electrodes before and after washing. Asphaltic and non asphaltic deposits were isolated, measured and analyzed.

3 Results and Discussion

As shown in Figure 2 (a, b), during electrodeposition tests white material was produced on water-immersed portion of the cathode with no dark deposits. On the other hand, no deposits were observed on water-immersed portion of the anode. However, dark deposits were attached to oil-immersed portion of the anode when it was withdrawn out of the oil at the end of each run. Some of deposited material on the electrodes was removed and lost in the oil when electrodes were withdrawn from the oil. Large agglomerates of the anodic deposits were suspended near the anode after electrodeposition tests. The particles which moves in the oil could not be seen because of opacity of the crude oil.

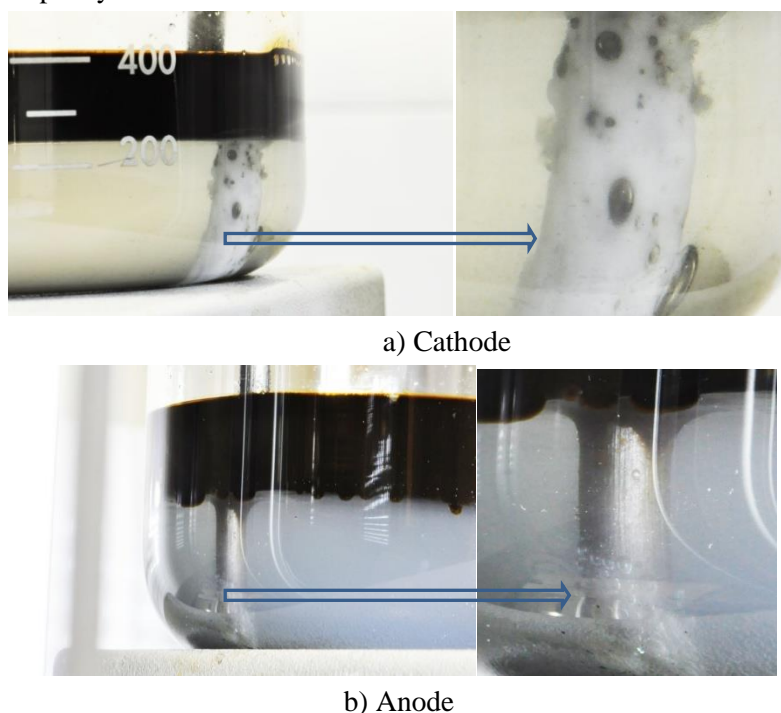


Figure 2: Electrodes appearance during experiment

when inspecting dried electrodes, a dark material was bounded to the anode while a white material was bounded to the cathode as illustrated in Figure 3 (b, c). The white material has yellowish color because the cathode was withdrawn through the oil portion. It is suggested that the dark deposits composed of asphaltene and non-

asphaltic particles with current net negative charges since the electrode was connected to the positive output of the power supply while the white deposits composed of non-organic particles with current net positive charges since the electrode was connected to the negative output of the power supply.

In addition, these results confirm that the presence of formation water with crude oil is essential to stimulate electrodeposition.

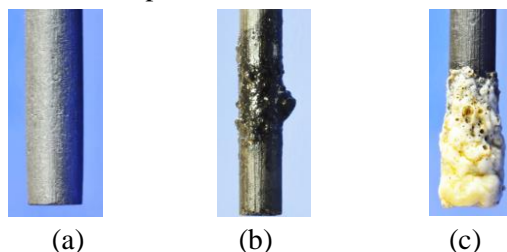


Figure 3: Electrodes appearance After experiment: (a) clean graphite electrode (b) anode (c) cathode

Figure 4 below shows a comparison of 3 runs under the same operating conditions but with different three current densities (10,20, and 30 A/m²) applied to a mixture of crude oil and formation water of 240K ppm salinity and 60% water cut. The plotted data of asphaltene mass against run time reveal the effect of time on amount of asphaltene deposition. The mass of the asphaltene deposits increased with time. The rate of deposition is fast below 10 hrs and it becomes slower above 10 hrs. Run time has no effect on the charge of the deposit.

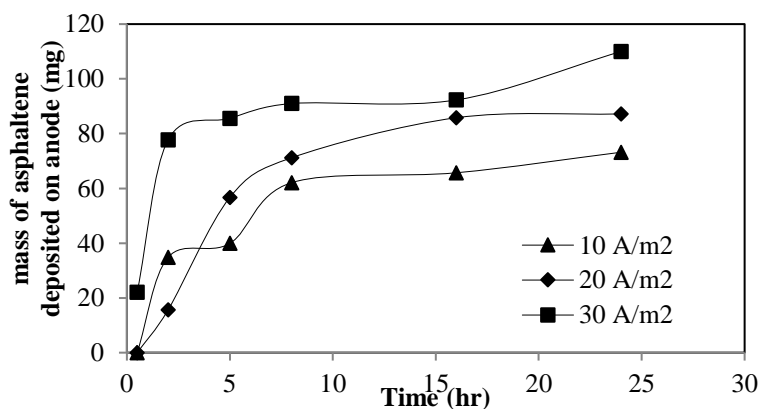


Figure 4: Effect of run time and current density on asphaltene deposition

The percentage of asphaltene arrested on the anode from the original asphaltens contained in crude oil sample was shown in Figure 5. The figure reveals that the maximum amount arrested on the anode from the original asphaltic material in crude oil sample was 18% for current density of 30 A/m² and duration of 24 hours.

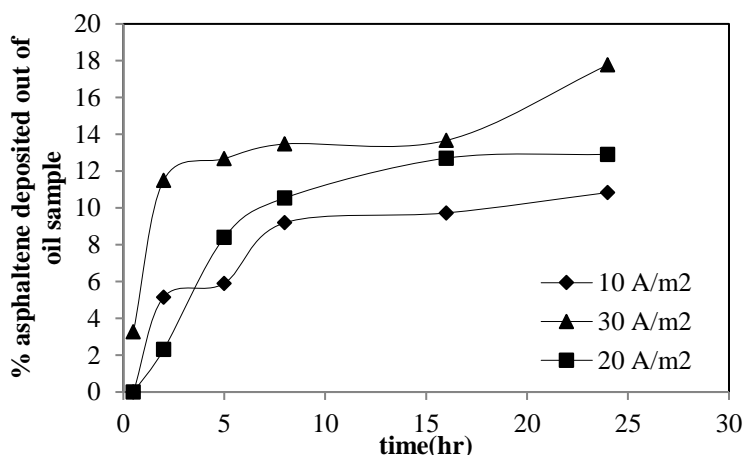


Figure 5: Asphaltene percentage arrested versus run time

Figure 6 and Figure 7 are showing the effect of three different current densities on amount of deposition on both anode and cathode for two run times (8hrs, and 16 hrs). The deposit on both the cathode and the anode has increased with higher current density. As the current density increased, a gradual increase in anodic deposition was observed; however, higher current density resulted in a dramatic increase in cathodic deposition. Current density has no effect on the charge of the deposit.

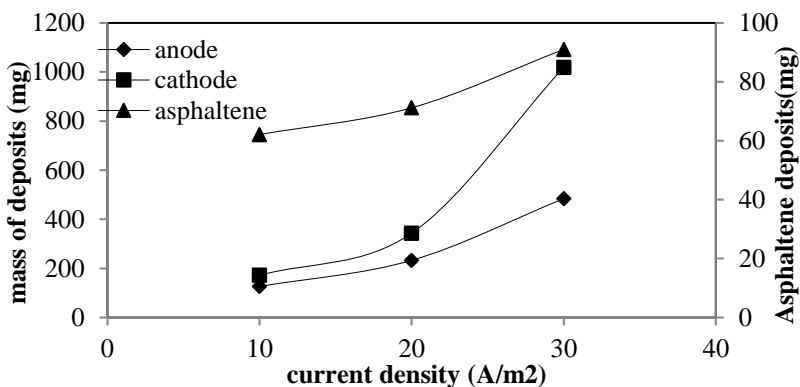


Figure 6: Effect of current density on deposition after 8 hrs

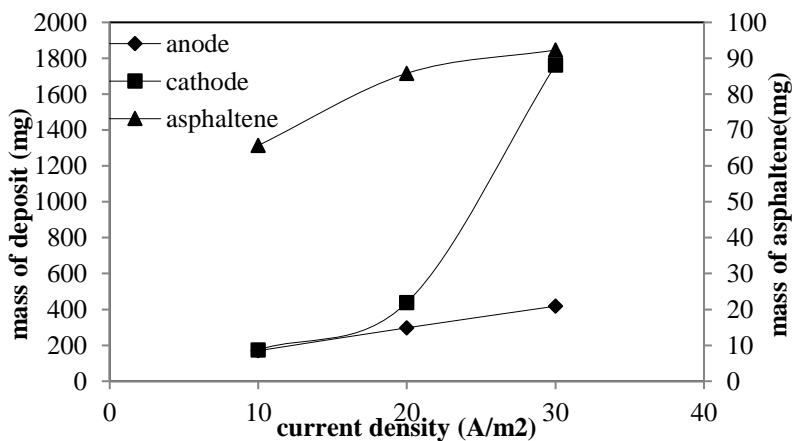
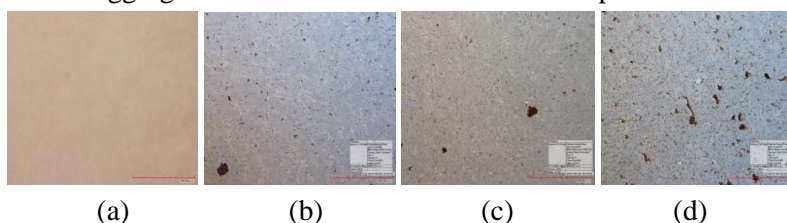


Figure 7: Effect of current density on deposition after 16 hrs

The above results will be utilized to evaluate the kinetics of asphaltenes deposition from Abu Dhabi crude oils and formulate a kinetic model that fits the data to correlate the amount of deposits with operating parameters. This will identify the optimum operating conditions of the electrodeposition process to arrest the maximum percentage of asphaltic and non-asphaltic materials from crude oil.

3.1 Microscopic images

The microscopic images of the crude oil were compared before and after electrodeposition. Figure 8(a) shows the microscopic image of a blank crude oil sample before electrodeposition and images of crude oil samples after electrodeposition (b,c,d) at a current density of 10, 20, and 30 A/m² respectively. As shown by the figures, it was obvious that there were some asphaltene particles in the destabilized crude oil. Asphaltenes in crude oil was destabilized in the presence of formation water by the applied DC current. The dark spots in the images indicated the presence of asphaltene in crude oil. It is clear that as the current density increases more asphaltene aggregates were found in the crude oil sample.

**Figure 8:** Crude oil images before deposition and after electrodeposition at 10, 20 and 30 A/m²

3.2 Analysis of Asphaltene Deposition

Since it was obvious that there were deposits on the anode, it was necessary to isolate the asphaltic material from the non-asphaltic deposit and then analyze it using SEM images.

After deposits were washed with toluene (0.5-1.0 g in 100 ml toluene), the washed deposits in toluene were centrifuged at 4000 rpm speed for five minutes. The supernatant were collected and concentrated by evaporation overnight in the fume hood. After estimating the toluene solution volume then asphaltene was precipitated with 40 times that volume of n-heptane. The solution was centrifuged and the supernatant was discarded while centrifuged asphaltene solids were left to dry for several days or when the change in the container weight was < 0.0001 g. Asphaltene solids were analyzed by SEM.

The asphaltene solids were analyzed by SEM imaging > 1000× magnifications for different operating conditions. In Figure 9, the microscopic structures of C₇-asphaltenes show irregular porous surfaces with pore sizes of several microns.

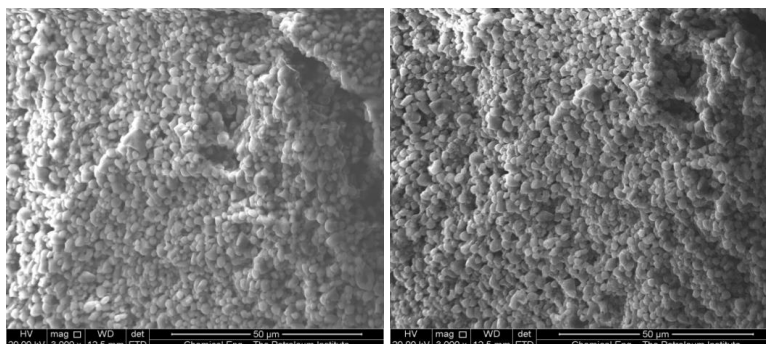


Figure 9: SEM images for asphaltene deposits

While the morphological elemental compositions are shown in Figure 10 and the deposits mainly contain C, S, O, N and Cr, Cu, Al, Si, Ni, Pt. This analysis confirms the different components of asphaltene as a complex blend.

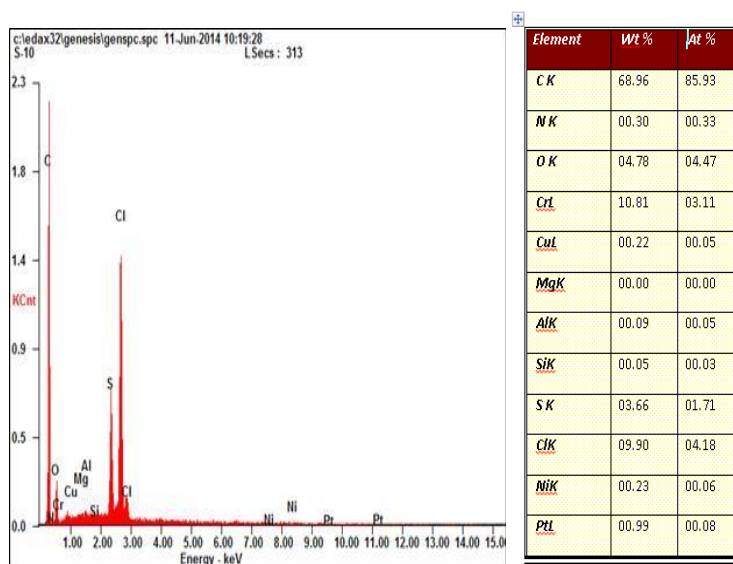


Figure 10: Elemental analysis for asphaltene deposits

Inorganic deposits were analyzed by SEM imaging. Figure 11 shows the morphology for the inorganic deposits on the cathode. Some of asphaltic/non asphaltic materials in the oil were attached to the cathode when the electrode was withdrawn from the oil. Figure 12 demonstrates the elemental analysis of the inorganic deposits obtained which contains Na, Ca, Mg, Cl and carbon.

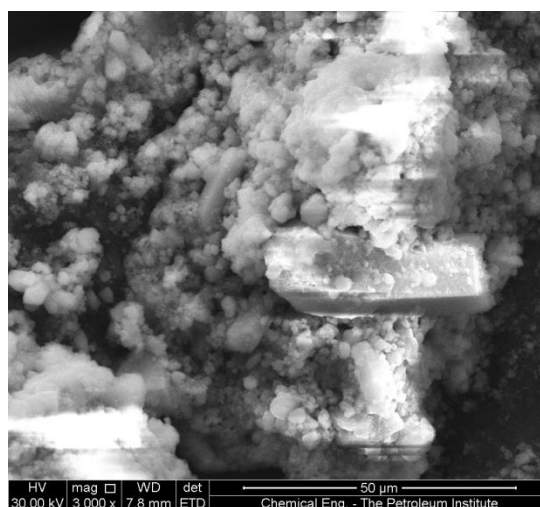


Figure 11: SEM images for inorganic deposits

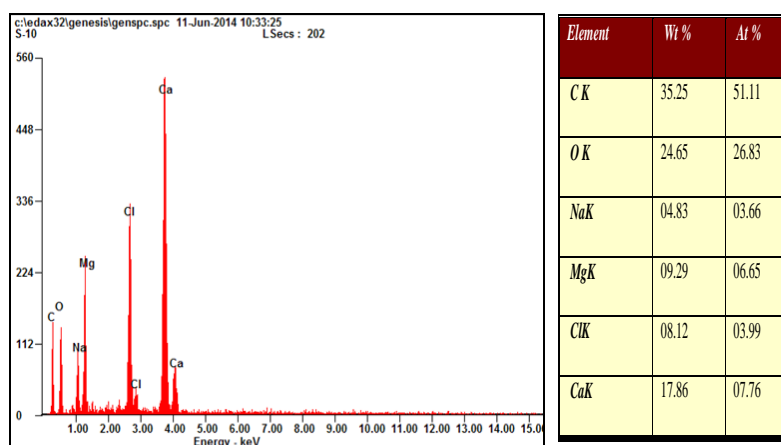


Figure 12: Elemental analysis for inorganic deposits

4 Conclusions

Results confirm that the presence of formation water with crude oil is essential to stimulate electrodeposition. As the current density increased, a gradual increase in anodic deposition was observed; however, higher current density resulted in a dramatic increase in cathodic deposition. Experiment time and current density play a crucial role on deposition rate. With higher current density at experiments times below 10 hrs, deposits were arrested on the electrodes with a faster rate. Deposits composed of asphaltene and non-asphaltic particles have negative charge. No charge alterations noticed with increasing run time and current density. The maximum amount of asphaltic material arrested on the anode from the original asphaltic material in crude oil sample was 18% for current density of 30 A/m² and duration of 24 hours. The results obtained will be utilized to develop a kinetic model that relates amount of asphaltenes deposited with various operating conditions. This will help to identify the optimum operating conditions of the electrodeposition process to arrest the maximum percentage of asphaltic and non-asphaltic materials from crude oils.

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